

APPROXIMATE ATOMIC WEIGHTS OF COMMON ELEMENTS

Element	Symbol	Atomic Weight	Element	Symbol	Atomic Weight
Aluminum.....	Al	27	Lead.....	Pb	207
Antimony.....	Sb	122	Lithium.....	Li	7
Arsenic.....	As	75	Magnesium.....	Mg	24
Barium.....	Ba	137	Manganese.....	Mn	55
Beryllium.....	Be	9	Mercury.....	Hg	200
Bismuth.....	Bi	209	Nickel.....	Ni	59
Boron.....	B	11	Nitrogen.....	N	14
Bromine.....	Br	80	Oxygen.....	O	16
Cadmium.....	Cd	112	Phosphorus.....	P	31
Cesium.....	Cs	133	Platinum.....	Pt	195
Calcium.....	Ca	40	Potassium.....	K	39
Carbon.....	C	12	Radium.....	Ra	226
Chlorine.....	Cl	35.5	Rubidium.....	Rb	85
Chromium.....	Cr	52	Silicon.....	Si	28
Cobalt.....	Co	59	Silver.....	Ag	108
Copper.....	Cu	63.5	Sodium.....	Na	23
Fluorine.....	F	19	Strontium.....	Sr	88
Gold.....	Au	197	Sulfur.....	S	32
Hydrogen.....	H	1	Tin.....	Sn	119
Iodine.....	I	127	Tungsten.....	W	184
Iron.....	Fe	56	Zinc.....	Zn	65

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Clifford J. Garner
U.C.L.A.
15 March 1948

Mass of Proton
= 1.00759 amu

Mass of Neutron = 1.00866 amu

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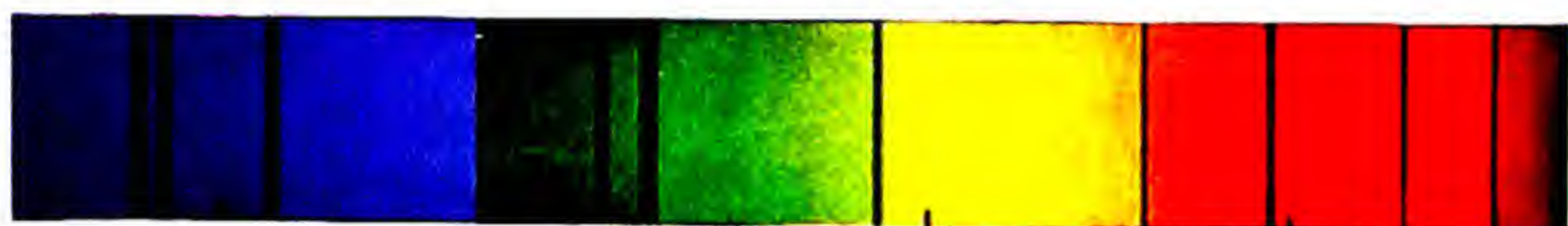
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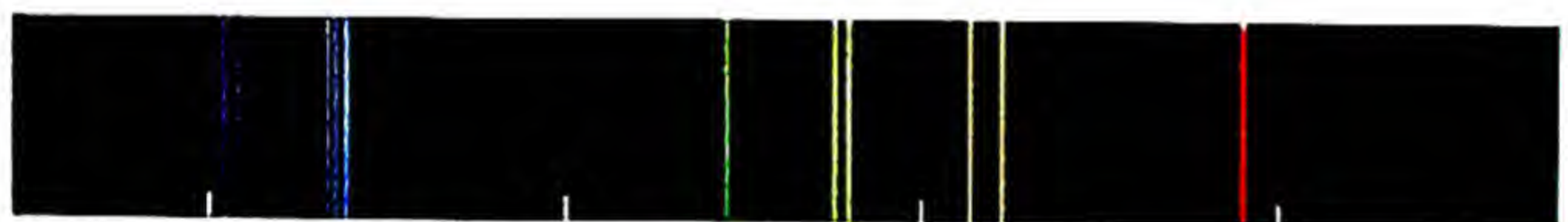
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SPECTRA

Every chemical element, whether on the earth or in a distant part of the universe, reveals its identity by its spectrum. Besides the colored lines disclosed to the eye by means of the spectroscope, most of the elements have many others lying beyond the visible region in both directions.

≡ GENERAL ≡ CHEMISTRY

A First Course

BY

L. E. YOUNG

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UNIVERSITY OF CALIFORNIA

REVISED EDITION

New York

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Preface to the Revised Edition

IN THIS REVISION we have been guided by suggestions from many teachers who are using the book and who are interested in its improvement. The principal changes which have been made may be summarized as follows:

Chemical symbols, formulas, and equations are introduced earlier in the course. The use of equations has been advanced from Unit IV to Unit II.

Physical properties of families of elements are summarized in tables for easy reference.

The gas laws are assembled and fully developed where the first use for them appears, and Graham's law of diffusion is included. In the earlier edition the major treatment of the gas laws was found in an appendix at the end of the text.

Raoult's law is formulated and relationships between vapor pressure, freezing point, boiling point, and osmotic pressure are illustrated.

A section on crystallization and crystal forms has been added.

Many technical developments of popular interest have been explained. Among these are the methods of making nylon, rubber, and "high octane" gasoline.

The section dealing with organic compounds has been expanded, and the chemistry of foods and vitamins is now presented in sufficient detail to be of interest to students of dietetics and nursing.

L. E. Y.
C. W. P.

Preface to the First Edition

IN THIS BOOK the fundamental principles of chemistry are explained in simple language, and illustrative matter is drawn from the experiences of daily life. An elementary discussion of atomic structure is presented early, for we have found that students have an unusual interest in this subject. Supplementary reading is provided for students who have the habit of exploring realms beyond the limits of prescribed work. The supplement will not ordinarily be assigned for study. Students who can profit by this section of the book will need no classroom reference to it.

A balance between theoretical and applied science has been maintained throughout the text. It has been our aim to present enough chemical theory to stimulate the imagination, and, at the same time, to create an interest in modern industrial processes.

The entire manuscript was read by W. M. Latimer of the University of California; Douglas W. Bowden of Stuyvesant High School, New York; and Z. T. Walter of Los Angeles City College. Parts of the manuscript were read by William E. Morrell of Wright Junior College, Chicago; Bailey W. Howard of Pasadena Junior College; H. J. King of Fresno State College; and H. V. Tartar of the University of Washington. We take this opportunity to thank them for their valuable suggestions. We desire also to express our appreciation of the work of our draftsman, A. Rollins King.

THE AUTHORS

Contents

PART	PAGE
PREFACE TO THE REVISED EDITION.	v
PREFACE TO THE FIRST EDITION	vi
INTRODUCTION.	1

Unit I

MATTER AND ENERGY; COMPOUNDS, ELEMENTS, AND MIXTURES

1. THE NATURE OF MATTER.	4
2. COMPOUNDS, ELEMENTS, AND MIXTURES	8
3. PHYSICAL STATES OF MATTER; CRYSTALS.	17
4. PROPERTIES OF MATTER AND ENERGY: CHEMICAL AND PHYSICAL CHANGES.	25

Unit II

THE ATMOSPHERE; OXYGEN, HYDROGEN, WATER; SOLUTIONS AND GAS LAWS

1. THE ATMOSPHERE	32
2. OXYGEN	39
3. HYDROGEN	52
4. WATER; HYDROGEN PEROXIDE.	63
5. SOLUTIONS	78
6. KINETIC THEORY	89
7. GAY-LUSSAC'S LAW; AVOGADRO'S LAW	99

Unit III

ATOMS, MOLECULES; THE ELECTRON THEORY; THE PERIODIC TABLE

1. ATOMS; ATOMIC WEIGHTS; MOLECULAR WEIGHTS	103
2. THE ELECTRON THEORY	107
3. THE PERIODIC TABLE	117
4. STRUCTURE OF THE HEAVIER ATOMS	132

Unit IV

CHEMICAL EQUATIONS AND CHEMICAL CALCULATIONS

1. CHEMICAL EQUATIONS	136
---------------------------------	-----

PART	PAGE
2. CHEMICAL CALCULATIONS	146
3. CALCULATIONS INVOLVING THE WEIGHTS OF GASES	156
4. CALCULATIONS INVOLVING GRAM-MOLECULAR VOLUMES	160

Unit V

GROUP I OF THE PERIODIC TABLE: THE ALKALI METALS

1. SODIUM	164
2. POTASSIUM, LITHIUM, RUBIDIUM, AND CESIUM	172
3. THE PHOTOELECTRIC EFFECT; SPECTRUM ANALYSIS	175

Unit VI

GROUP VII OF THE PERIODIC TABLE: THE HALOGENS AND
HALOGEN ACIDS

1. CHLORINE	180
2. FLUORINE, BROMINE, AND IODINE	187
3. HYDROCHLORIC ACID	193
4. HYDROFLUORIC ACID; HYDROBROMIC ACID; HYDRIODIC ACID	198
5. OXYGEN COMPOUNDS OF THE HALOGENS	203

Unit VII

ACIDS, BASES, AND SALTS; IONIZATION; COLLOIDS

1. ACIDS, BASES, AND SALTS	207
2. IONIZATION: CONDUCTORS AND NONCONDUCTORS OF ELECTRICITY	214
3. EQUATIONS FOR REACTIONS INVOLVING IONS	226
4. STANDARD SOLUTIONS; TITRATIONS	232
5. COLLOIDS	237

Unit VIII

GROUP V OF THE PERIODIC TABLE: NITROGEN, PHOSPHORUS,
ARSENIC, ANTIMONY, AND BISMUTH

1. NITROGEN	246
2. AMMONIA	252
3. OXIDES AND ACIDS OF NITROGEN	259
4. OXIDATION AND REDUCTION	266
5. SPEEDS OF CHEMICAL REACTIONS	272
6. OTHER MEMBERS OF GROUP V	275
7. ACIDS OF PHOSPHORUS	280
8. ARSENIC, ANTIMONY, AND BISMUTH	284

Unit IX

GROUP IV OF THE PERIODIC TABLE: CARBON, SILICON, TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM

PART	PAGE
1. CARBON	288
2. OXIDES AND ACIDS OF CARBON.	295
3. SALTS OF CARBONIC ACID.	308
4. SILICON AND ITS COMPOUNDS	311
5. TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM.	321

Unit X

GROUP VI OF THE PERIODIC TABLE: SULFUR, SELENIUM, AND TELLURIUM

1. SULFUR.	323
2. THE SULFIDES.	329
3. OXIDES AND ACIDS OF SULFUR.	333
4. SELENIUM AND TELLURIUM AND THEIR COMPOUNDS	342

Unit XI

GROUP II OF THE PERIODIC TABLE: BERYLLIUM, MAGNESIUM, CALCIUM, STRONTIUM, BARIUM, AND RADIUM

1. BERYLLIUM AND MAGNESIUM	344
2. CALCIUM AND ITS COMPOUNDS.	349
3. HARD WATER AND ITS SOFTENING	354
4. STRONTIUM, BARIUM, AND RADIUM.	359

Unit XII

GROUP III OF THE PERIODIC TABLE: BORON AND ALUMINUM

1. BORON.	364
2. ALUMINUM	367
3. AMPHOTERIC SUBSTANCES.	373

Unit XIII

SUBGROUP I OF THE PERIODIC TABLE: COPPER, SILVER, AND GOLD

1. COPPER.	375
2. SILVER.	382
3. GOLD.	389
4. COMPLEX IONS OF COPPER AND SILVER WITH AMMONIA	392

Ch

CONTENTS

Unit XIV

SUBGROUP II OF THE PERIODIC TABLE: ZINC, CADMIUM, AND
MERCURY

PART	PAGE
1. ZINC	394
2. CADMIUM AND MERCURY	400

Unit XV

ELECTROMOTIVE SERIES; ELECTRIC CELLS; STORAGE BATTERIES;
ELECTROLYSIS; ELECTRODE POTENTIALS

1. THE ELECTROMOTIVE SERIES	404
2. ELECTRIC CELLS	408
3. STORAGE BATTERIES	412
4. ELECTROLYSIS	415
5. ELECTRODE POTENTIALS	419

Unit XVI

SUBGROUP IV OF THE PERIODIC TABLE: GERMANIUM, TIN, AND
LEAD

1. GERMANIUM AND TIN	421
2. LEAD	426

Unit XVII

SUBGROUP VI OF THE PERIODIC TABLE: CHROMIUM,
MOLYBDENUM, TUNGSTEN, AND URANIUM

1. CHROMIUM	431
2. MOLYBDENUM, TUNGSTEN, AND URANIUM	434

Unit XVIII

SUBGROUP VII OF THE PERIODIC TABLE: MANGANESE AND
RHENIUM

1. MANGANESE	437
------------------------	-----

Unit XIX

IRON, COBALT, NICKEL, AND THE PLATINUM FAMILY

1. IRON	439
2. COBALT AND NICKEL	452
3. THE PLATINUM METALS	455

Unit XX

CARBON COMPOUNDS

PART		PAGE
1.	THE HYDROCARBONS.	459
2.	HALOGEN COMPOUNDS AND ALCOHOLS	474
3.	ALDEHYDES, KETONES, AND ACIDS.	479
4.	ESTERS AND ETHERS.	482
5.	CARBOHYDRATES.	484
6.	FUELS	487

Unit XXI

PLANT AND ANIMAL LIFE

1.	ELEMENTS ESSENTIAL TO PLANT LIFE	490
2.	COMPOUNDS ESSENTIAL TO ANIMAL LIFE	494

Unit XXII

RADIOACTIVITY AND THE TRANSMUTATION OF ELEMENTS

1.	RADIOACTIVE ELEMENTS	504
----	--------------------------------	-----

APPENDIX

THE METRIC SYSTEM.	511
VAPOR PRESSURES OF WATER.	513
WEIGHT OF ONE LITER OF VARIOUS GASES	514
MELTING POINTS OF METALS AND A FEW NONMETALS	514
OXIDATION-REDUCTION POTENTIALS	514
PROPERTIES OF SULFIDES.	515
INDEX	517

Introduction

We are living in a chemical age, and we are surrounded by products of the laboratory. Let us pause to think of a few ways in which the science of chemistry has affected our lives. What useful or enjoyable things have we derived from laboratory studies? To what extent has chemistry been responsible for the ordinary comforts and conveniences that are ours today?

Matches were a novelty to our great-grandparents. For centuries fire was created by striking stones together, and when a fire was started in a stove or a fireplace, it was carefully tended, day and night, lest it go out. When it was extinguished, fire was borrowed from a neighbor, or it was supplied by a "keeper of the fires"—a person whose duty it was to keep a fire burning day and night, winter and summer, for the benefit of others in the community. Then a chemist invented matches. Now, we strike a match when we are ready for fire, and we no longer regard the match as a novelty or as an important invention.

The gaseous and liquid fuels, upon which we are so dependent, were developed by chemical methods. Imagine the difficulties of an automobile trip across the country with an engine dependent upon wood or coal for fuel.

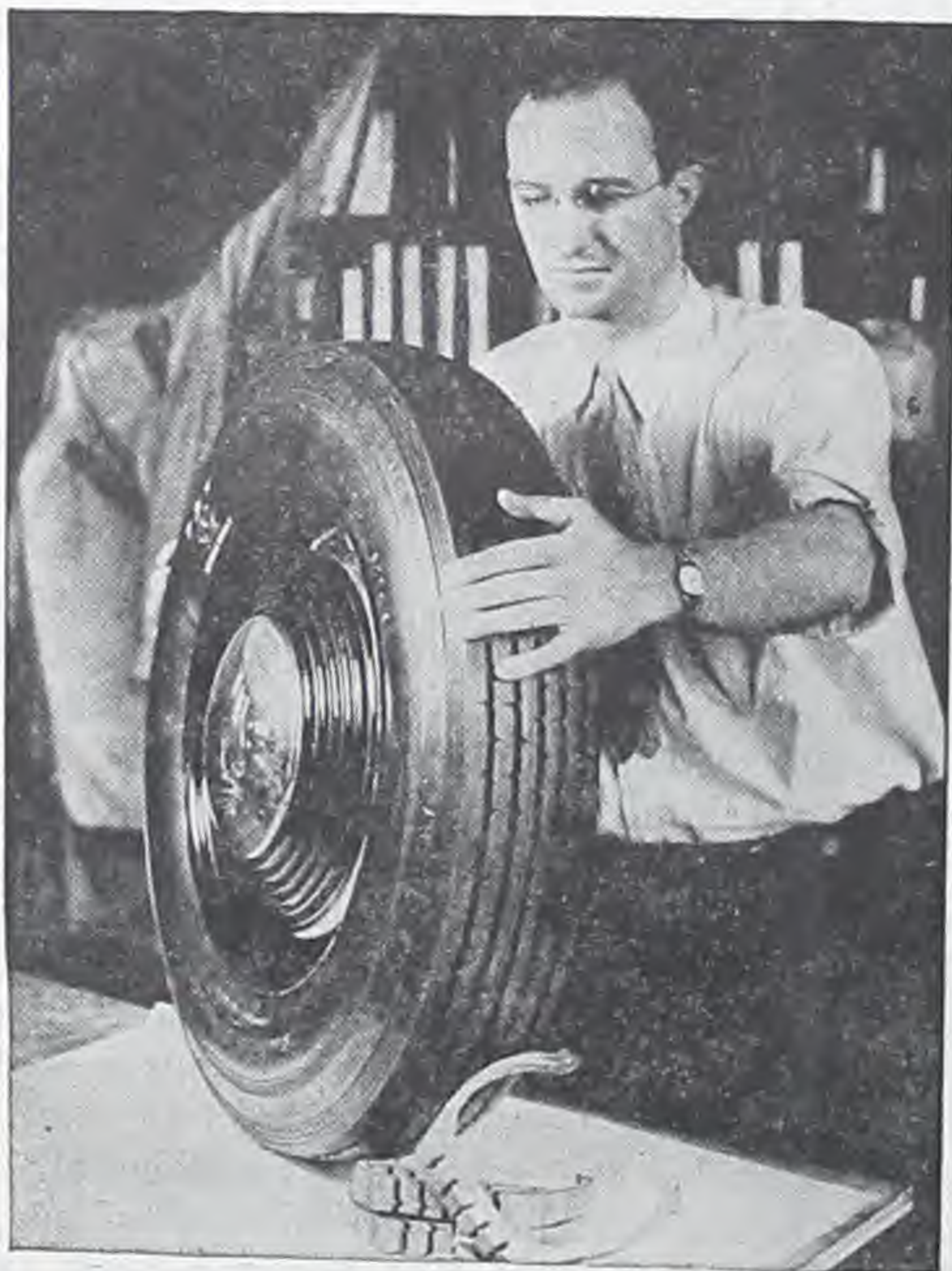
The dyes with which our clothes are made attractive and colorful were obtained by chemists from products contained in a black, sticky tar formed in the distillation of coal. Silk was formerly worn only by the wealthy. Now, equally attractive articles made of rayon or nylon, artificial textiles, are within the reach of all. Most of our perfumes and flavorings are artificial products of the chemical laboratories, and many of our foods and beverages are made or modified by chemical processes. Baking powder is a synthetic preparation that is found in every kitchen.

Medicine and surgery have been promoted beyond measure by discoveries in chemistry. Operations were formerly performed without the aid of anesthetics or antiseptics, and no standardized drugs were available. The list of useful medicines is growing constantly as a result of researches carried on in chemical laboratories, and human suffering is relieved by safe methods in the hospitals of all civilized countries.

Our electric light bulbs give a brilliant light and have a long life because twentieth-century chemists explored the properties

of the element tungsten, which was discovered in 1783. We should not like to return to the candle or even the kerosene lamp.

The metals which we use daily are obtained from their ores through chemical methods. The production of light-weight metals aided greatly in the development of the airplane, and special types of steels (alloys) made the automobile a practical invention.



Courtesy, B. F. Goodrich Co.

Fig. 1. Synthetic rubber. Petroleum and alcohol are the main sources of the compounds used in making rubber.

Moving pictures, scenes transmitted by telegraph, and all other applications of the principles of photography are direct or indirect results of chemical experiments. Certain compounds are sensitive to light. Their chemical properties are altered by a momentary exposure to light. Such compounds are incorporated in photographic films, and through a series of chemical reactions, the latent images produced in such films by exposure to reflected light can be developed and made permanent.

These are but a few examples of the achievements of a chemical age. If we want to understand these things, and if we hope to

keep pace with the progress of science, we must become acquainted with the laws and theories of chemistry and physics. In this



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Fig. 2. Synthetic silk. Parachute troops depend upon the lightness and strength of nylon. This fine textile fiber is made from compounds containing carbon, hydrogen, oxygen, and nitrogen.

course we shall study the most important principles of chemistry and learn many practical ways of applying them.

UNIT I

Matter and Energy; Compounds, Elements, and Mixtures

PART 1

The Nature of Matter

What is matter? We are all acquainted with the common and most useful kinds of matter. The air we breathe, the water we drink, the cereal or toast we eat for breakfast, our salt, our meat, and our sugar are familiar forms of matter. Iron, gold, wood, soil, leather, and oil are other examples. There are thousands of kinds of *substances* in the world, and each substance represents a form of matter. *Anything that occupies space and has weight is matter.*

For ages the question was debated as to what makes up matter as we know it. If a piece of any substance, such as a block of wood or a rock, were divided in half, and if the half were cut in two, and so on an infinite number of times, what would remain? Some have believed that any substance could be divided an infinite number of times and still yield a smaller piece of the same sort of matter. Others have thought that the process of dividing a substance into smaller and smaller portions would lead, ultimately, to a particle that could not be cut in two.

The ancient Greeks, who were philosophers rather than scientists, speculated on the nature of matter. They realized that upon repeatedly dividing a pail of water they would finally have left a very small drop of the liquid, and they believed that if they should divide the drop into smaller parts, and each of these, in turn, into still smaller parts, and so on to a limit far beyond man's ability to separate them, there would be obtained, finally, a minute particle which could not be further divided. This particle they called an *atom*, meaning "something that cannot be cut."

Molecules. We may divide a drop of water into smaller drops, and divide each of the fragments into still smaller droplets. Let us imagine that the process of division could be continued indef-

initely, even with droplets too small to be seen. The time would come when we should obtain a particle which, if divided, would give rise to something different from water. This tiny particle (not visible with the aid of the most powerful microscope) would be a *molecule* of water. A visible drop of water contains millions of molecules.

Molecules are composed of smaller parts called *atoms*. If we were to break a *molecule* of water into smaller pieces, we should find the fragments of the molecule to be entirely different from the original substance. We should have atoms of two substances, hydrogen and oxygen. Each water molecule is composed of three atoms—two atoms of hydrogen and one atom of oxygen. The three atoms cling together so tightly that it takes an extremely high temperature or an electric current to separate them. A diagram representing the union of hydrogen and oxygen in water is shown in Fig. 3.

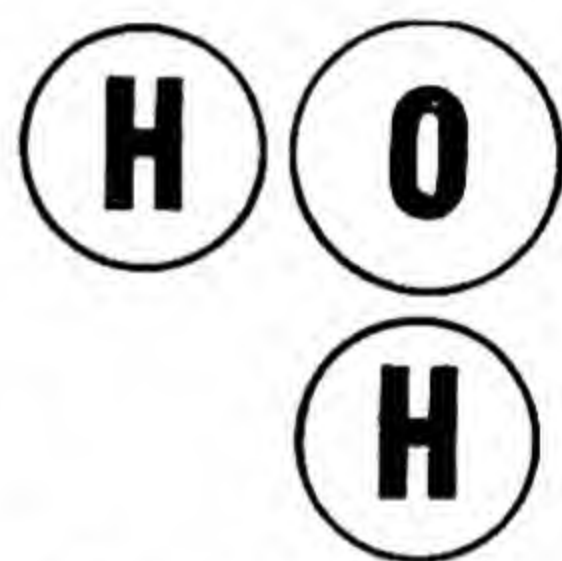


Fig. 3. A water molecule contains one atom of oxygen and two atoms of hydrogen.

Let us consider a crystal of table salt, which the chemist calls sodium chloride. We can break the crystal into a hundred pieces, and we can break each of these small fragments into a hundred pieces or more. Let us suppose that the process of subdivision could be continued at will. We should finally obtain the smallest particle of the substance which retains the properties of salt. We should, as in the case of water, have a single molecule of the substance, this time a molecule of sodium chloride. A single molecule of table salt would be so light that it could not be a solid substance. It would be a molecule of sodium chloride gas. If this molecule were decomposed, we should obtain atoms that in no way resemble the original molecule. Each molecule of sodium chloride gas is composed of two atoms: one is an atom of *sodium*, the other an atom of *chlorine*. The molecule may be represented as a combination of sodium and chlorine as shown in Fig. 4. In a crystal of common salt there are many thousands of sodium atoms and an equal number of chlorine atoms, so arranged that each sodium atom is surrounded by six chlorine atoms and each chlorine atom is surrounded by six sodium atoms. When the salt is heated to a temperature of 800°C . (1472° Fahrenheit) it melts and the regular pattern of the crystal is broken up. At a much higher temperature the liquid boils. Salt vapor escapes from the hot liquid just as water vapor escapes from hot water, and in the vapor state there is no orderly grouping of large numbers of atoms. The salt vapor consists of separate molecules of sodium

chloride, each molecule consisting of one atom of sodium and one atom of chlorine.

We have in common salt an excellent example of the difference between the properties of molecules of substances and the properties of the atoms from which the molecules are made. No living animal can survive without salt in its diet. Deer and other wild animals travel for miles to reach a salt lick. Every year many tons of rock salt are distributed on grazing areas in the United States so that the cattle will not suffer from a lack of salt. Hunters in Lapland and in northern Russia often use salt as a bait for reindeer. Yet the substances from which salt is formed are far from edible. Sodium is a metal so reactive that it is dangerous to handle. When it touches water, it sputters around and liberates a gas that may catch fire. Chlorine is a very evil-smelling gas which inflames the eyes, nose, and throat. Can you imagine using either of these substances as food? However, the compound formed from two

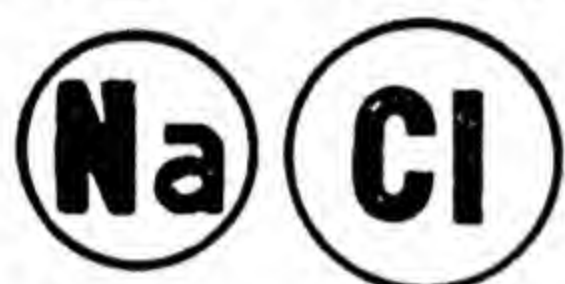


Fig. 4. In the vapor state a molecule of sodium chloride contains one atom of sodium and one atom of chlorine. For the arrangement of the atoms in a crystal of common salt, see page 24. For the condition of salt when dissolved in water, see pp. 216–217.

of these dangerous atoms is harmless and is an essential part of man's diet.

The molecule of sugar is larger and far more complex than the molecule of either water or salt. Ordinary sugar "burns" if heated, leaving a black residue which the chemist calls carbon. Water passes off during the heating process. Since we have learned that water is composed of oxygen and hydrogen atoms, sugar must contain atoms of three kinds: carbon, hydrogen, and oxygen. The smallest particle of sugar which can exist and still be sugar is actually composed of 12 atoms of carbon, 22 atoms of hydrogen, and 11 atoms of oxygen. This is the sugar molecule. It is, of course, very large in comparison with a molecule of water or of sodium chloride, but even at that millions of sugar molecules must be clumped together in a single particle to be visible in the field of a powerful microscope.

What kinds of molecules exist in the air we breathe? Air is largely a mixture of the molecules of two gases: oxygen and nitrogen. The single molecule of each of these gases is a tiny thing composed of two atoms. A molecule of oxygen and one of nitrogen are pictured in Figures 5 and 6. Every time we inhale we take millions of these molecules into our lungs. Some of the oxygen is caught by the hemoglobin in the blood, which carries it throughout the body, where it burns up waste tissue. The nitrogen molecules are all driven from the lungs again when we exhale.

The nature of atoms. What are these tiny things called atoms? What do they look like? Why are hydrogen atoms, oxygen atoms, and carbon atoms different from each other?

The atomic idea of matter, proposed by the ancient Greeks, was cast aside for fifteen centuries. At the beginning of the nineteenth century, a Manchester schoolmaster, John Dalton, again focused attention on atoms. He concluded that all the atoms of any element are exactly alike. All hydrogen atoms, he said, are alike, but an atom of oxygen is very different from one of hydrogen. Dalton thought that atoms have some means of clinging to each other to form molecules and that these molecules might be broken up again to yield the separate atoms. The atoms, on the other hand, he assumed, could never be broken or altered in



Fig. 5. A molecule of oxygen consists of two atoms of oxygen held firmly together. The formula for oxygen gas is O_2 .



Fig. 6. A molecule of nitrogen consists of two atoms of nitrogen held tightly together. The formula for nitrogen gas is N_2 .

any way. In other words, he considered atoms the most permanent things in the universe.

At the close of the nineteenth century we learned something new about atoms. We now know that they are composed of units of electrical energy: *electrons*, infinitesimal negative charges, millions of which run through wires to light our electric bulbs and ring our doorbells; *protons*, positively charged units; and in addition to these, *neutrons*, uncharged bundles of energy; and *positrons*, which are as small as electrons but positively charged.

For the present let us think of atoms, as Dalton did, as indivisible minute particles from which molecules are made.

Questions and Exercises

1. Name several varieties of matter.
2. Define the following words: (a) matter, (b) electron, (c) atom, (d) molecule.
3. How do molecules differ from atoms?
4. Which of the following are forms of matter: (a) air, (b) water, (c) mind, (d) brain, (e) heat, (f) ink, (g) clouds, (h) sky, (i) perfume?
5. How do you know that the following are forms of matter: (a) the sun, (b) air, (c) smoke, (d) water, (e) glass, (f) iron?
6. Give the general characteristics of atoms as described by Dalton.

PART 2

Compounds, Elements, and Mixtures

Compounds. We have learned that all matter is composed of molecules, and that molecules are made up of atoms which cling tightly to each other. We have found that a molecule of water consists of two hydrogen atoms and one oxygen atom, and that the sugar molecule contains atoms of carbon, hydrogen, and oxygen firmly bound together. Such substances—water and sugar—are called *compounds*, because their molecules contain different kinds of atoms. *A compound is composed of molecules that are all alike,* but each molecule of a compound contains at least two different kinds of atoms.* Alcohol, soda, borax, and benzene are other examples of compounds.

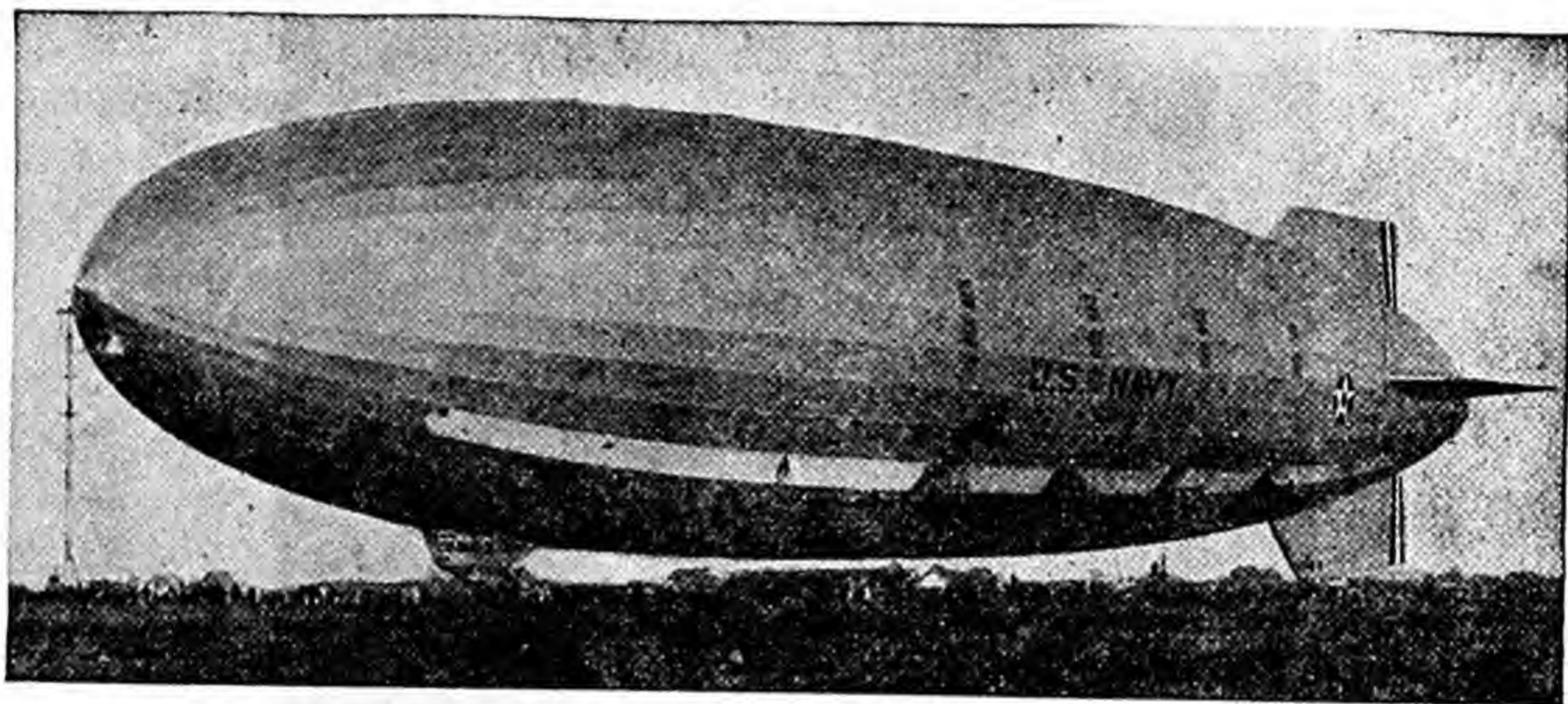
Elements. Elements, like compounds, exist in the form of molecules, but a molecule of an element is composed of atoms of one kind only.* The oxygen molecule consists of two oxygen atoms, firmly held together. Oxygen is an element, since its molecules contain atoms of one kind only; they are all oxygen atoms. Likewise, nitrogen is an element, because its molecules are made up of nitrogen atoms only. The chlorine molecule is composed of two chlorine atoms, the hydrogen molecule of two hydrogen atoms; hence chlorine and hydrogen also are elements. Iron, copper, gold, silver, platinum, sulfur, and carbon are all elements, since the molecule of each is composed of atoms of one kind only.

We may, for the present, define an element as a substance which cannot be decomposed and made to yield two or more different kinds of matter. A more exact definition, in terms of atomic structure, will be given later.

For centuries earth, air, fire, and water were believed to be elements from which everything else was made. When it was

* It is convenient to define a compound as a substance composed of molecules which are all alike. Similarly an element may be defined as a substance in which the atoms are all alike. Both definitions, however, require modification on account of the existence of isotopes. The nature of isotopes will be considered in connection with the electron theory.

proved that air is a mixture of gases, mainly oxygen and nitrogen, and that water can be broken up and made to yield two different gases, oxygen and hydrogen, then neither water nor air could be regarded any longer as an element. The true nature of fire was discovered in the eighteenth century, and fire was then discarded from the list of elements. We know now that earth is a mixture of many substances and, therefore, cannot be considered as an element.



Courtesy, U. S. Navy

Fig. 7. The dirigible type of airship created a demand for enormous quantities of helium.

Monatomic molecules. Although we usually find two or more atoms of the same kind combined to form a molecule of an element, there are some elements in which the atom prefers to remain alone. Helium is such an element. Helium is the extremely light gas which is used instead of hydrogen for filling dirigibles. The gas is obtained from springs or gas wells in Texas and Oklahoma. The United States owns nearly all the helium so far found on the earth. The molecule of helium is composed

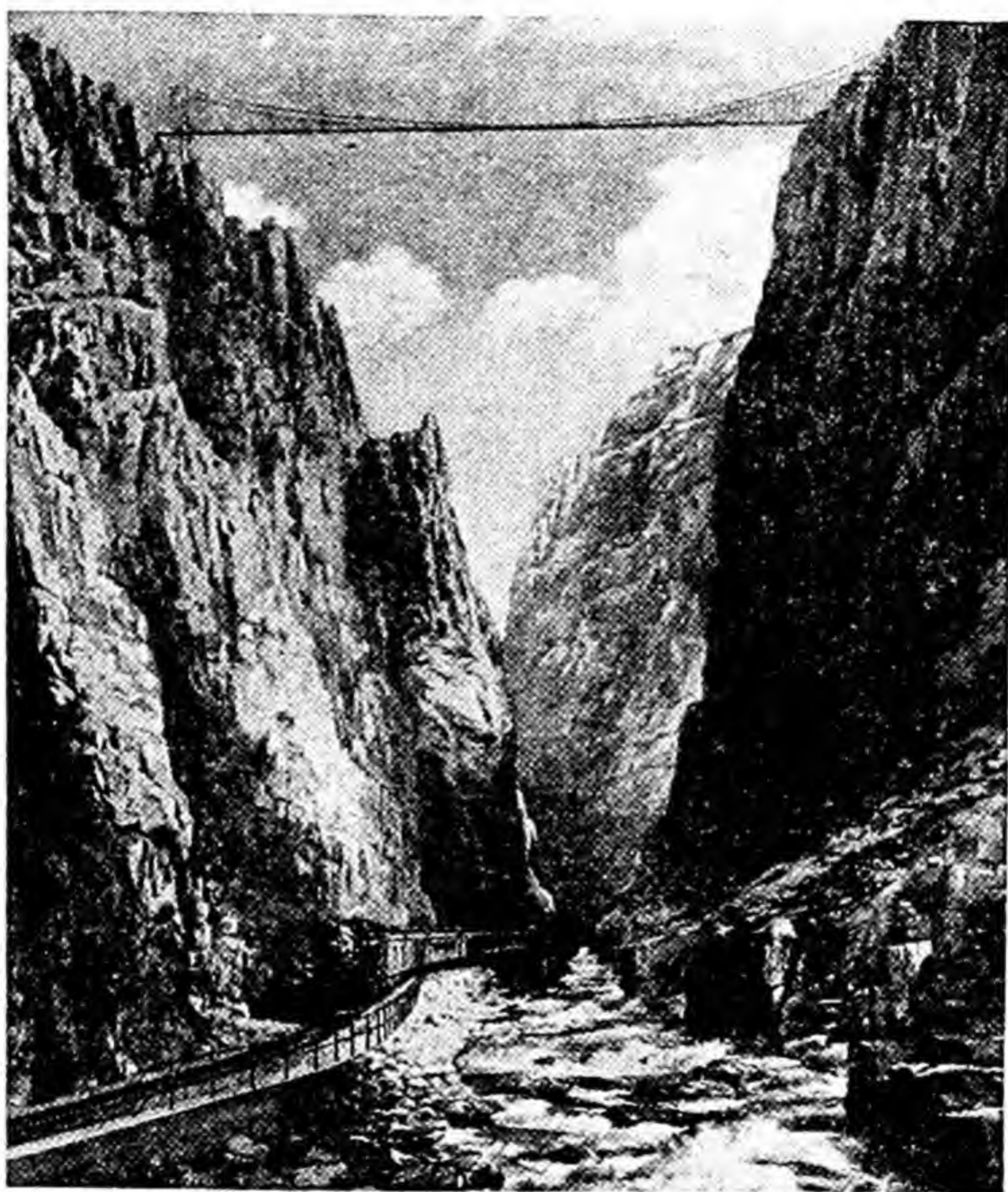
Fig. 8. The helium molecule consists of a single atom of helium. The formula for helium gas is He.



of a single helium atom. The gas is never found with pairs of atoms in the molecule, as are other common gases such as oxygen, nitrogen, hydrogen, and chlorine.

Neon gas, the name of which is familiar to all of us who have seen the bright neon lights at night, has but one atom in the molecule. Argon gas and mercury vapor, which with neon constitute the gas mixture in the blue and green neon signs, are also monatomic gases; that is, they have but one atom in the molecule.

The number of elements. Ninety elements have been discovered up to the present time, and chemists have reason to believe that there are no more than 92 or possibly 93 elements in the universe. From this relatively small number of elements are made the thousands of compounds known today. This vast variety is not surprising when we realize that the atoms are merely the blocks of which molecules are built. We might compare the



Courtesy, Denver & Rio Grande Western Railroad

Fig. 9. The Royal Gorge of the Arkansas River, Colorado. Erosion enables us to study the composition of the earth's crust to a depth of several thousand feet.

elements with the letters of the alphabet. A glance at any dictionary shows us the thousands of different words that can be formed from our 26 letters. Similarly, thousands of compounds may be formed from 92 elements.

Relative abundance of the elements. It might be supposed that the 92 elements would be evenly distributed over the earth, but such is not the case. Some of them are so rare that even the majority of chemists have never seen them. A list of 86 elements is given on the back cover of this book. Many of the names are familiar to all of us—iron, copper, silver, gold, platinum,

sulfur, oxygen, hydrogen, helium, aluminum, lead, nickel, nitrogen, tin, zinc, and radium. Many of them are unfamiliar, but are parts of substances which we see or use in everyday life. Some of us have never heard of silicon, but we have all seen ordinary sand, which is a compound containing silicon atoms and oxygen atoms. Calcium is an element which with carbon and oxygen is found in marble and limestone. Compounds of arsenic are used in medicines and as insect poisons. Boron is one of the elements in the well-known substances borax and boric acid. Carbon occurs in all living matter, both plant and animal. Lampblack and charcoal are almost pure carbon. A diamond is pure carbon in the crystalline form. The tiny filaments in our electric light bulbs are made of the element tungsten.

Although the element oxygen makes up nearly half of our known world, it was not discovered until 1774. The element silicon comprises approximately one-fourth of the crust of the earth of which we have any knowledge. Geologists say that the earth's crust, which contains all the known elements, either free or in the form of compounds, is many miles thick; but, since our deepest mines penetrate only about two and a half miles into this crust, the composition of the remainder is really unknown. We can only guess that it is similar to the parts of the earth we actually know.

The relative proportions of the most abundant elements on the earth are shown in the following table. It includes those in the solid crust of the earth, the oceans, and the atmosphere.

THE PERCENTAGES BY WEIGHT OF THE MOST ABUNDANT ELEMENTS ON THE EARTH

Element	Per cent by weight	Element	Per cent by weight
Oxygen.....	50.02	Sodium.....	2.36
Silicon.....	25.80	Potassium.....	2.28
Aluminum.....	7.30	Magnesium.....	2.08
Iron.....	4.18	Hydrogen.....	0.95
Calcium.....	3.22	All others.....	1.81

How the elements are named. The question is often asked, "Who named the elements?" Usually the one who discovers an element gives it a name; but the sources of some of the names, such as iron, gold, and silver, are unknown. Sulfur was called "brimstone" in early times. It is referred to in the Bible as brimstone. Many elements have been named because of some

striking property. The name bromine means "bad smell," and all who have handled bromine agree as to its unpleasant odor. Some elements were named for countries, as germanium and columbium; some for heroes or gods, such as thorium, tantalum, and mercury.

The symbols of the elements. Chemists have adopted a sort of shorthand method for writing the names of the elements. In many cases this abbreviation, called the *symbol*, is the first letter of the name.

Element	Symbol	Element	Symbol
Hydrogen.....	H	Sulfur.....	S
Oxygen.....	O	Iodine.....	I
Nitrogen.....	N	Argon.....	A
Carbon.....	C	Phosphorus.....	P

Several of the elements have names commencing with the same letter, and it would lead to confusion if we did not discriminate between them in some way. This is done by choosing as the symbols for some of the elements two letters in the name. The name of the element calcium begins with C, but this symbol had been given to carbon before calcium was known. Hence, calcium is represented by the first two letters of the name, Ca, the C alone being capitalized. Cadmium has the same two first letters as calcium, and it would be confused with calcium if these letters were used as its symbol; so we use for cadmium the symbol Cd. Cobalt is represented by Co. Chlorine is represented by Cl, the first two audible letters in its name. Similarly, helium has the symbol He because the letter H had previously been chosen for hydrogen.

In order to avoid confusion in other cases, the symbols are derived from the first letter or letters of the Latin names of the elements. The symbol chosen for iron is Fe, the first two letters of its Latin name, *ferrum*. These easily distinguish it from iodine, whose symbol is I. Since S has been chosen as the symbol for sulfur, the symbol Na is used for sodium—the Latin name for sodium being *natrium*. Potassium has the symbol K, from the Latin *kalium*, in order to distinguish it from phosphorus, P. The table of the elements on the back cover shows the symbols of all the elements.

Mixtures. While discussing elements, we said that earth could not be an element because it is a mixture of many substances. It is made up of thousands of compounds, some of which are sand,

limestone, marble, clay, iron oxide, granite, and ores of various kinds. An *ore* is a compound of a metal with some other element or elements, or a mixture of minerals containing a free or a combined metal. Many of the elements occur in the earth's crust in the free state—that is, as the pure element—as well as in compounds. Among these are carbon and the metals gold, silver, copper, platinum, and lead. Sulfur also is found free in nature, in large deposits, especially in the neighborhood of volcanoes.

The earth cannot be classed either as an element or as a compound, for it is composed of many kinds of substances with many different kinds of molecules. We have defined a compound as a substance in which all the molecules are of the same kind. Since

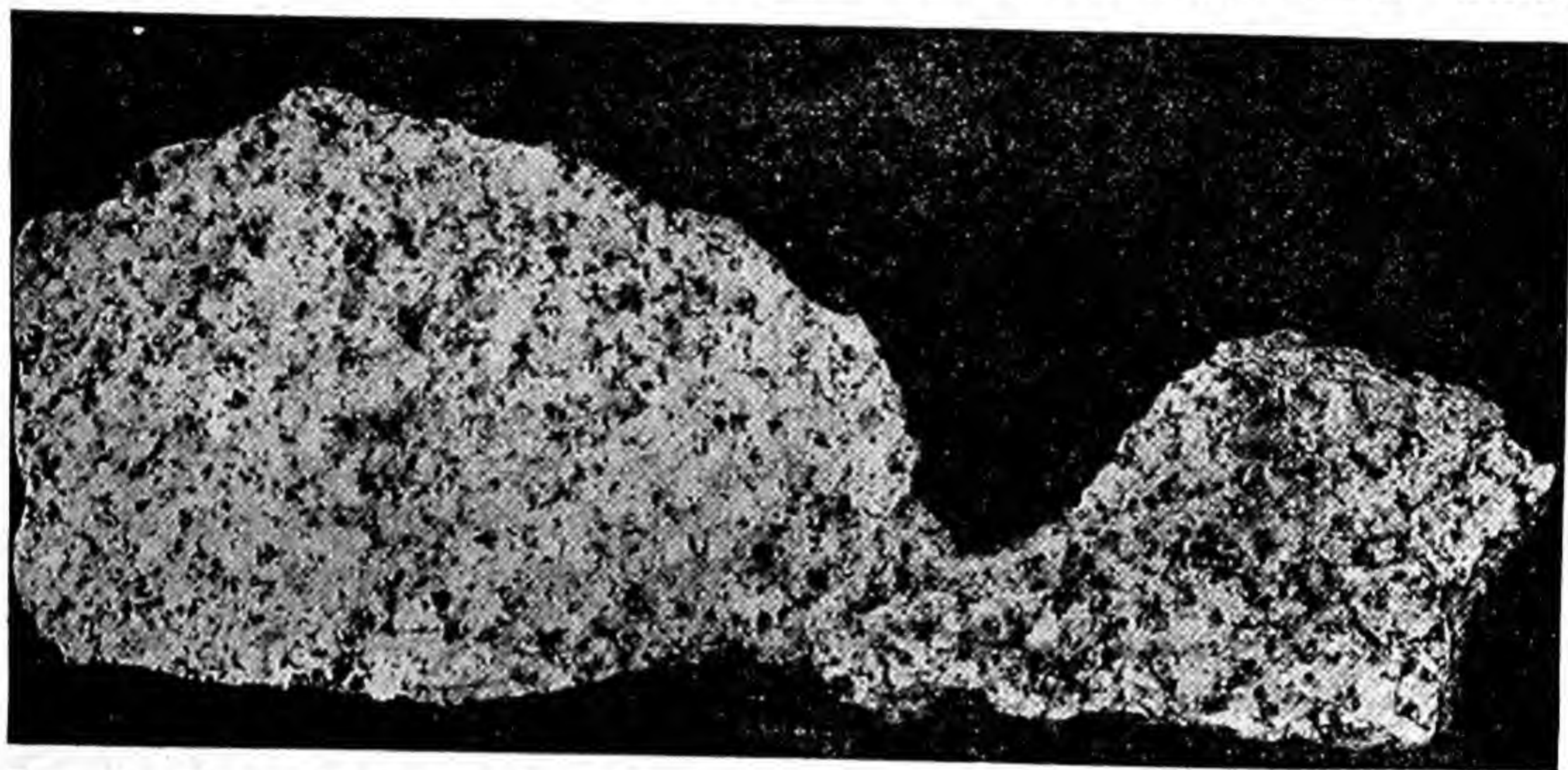


Fig. 10. The smaller piece of granite contains more mica (the black particles) than does an equal weight of the larger piece.

earth has many kinds of molecules in it, it must be a mixture. A *mixture is matter composed of two or more different kinds of molecules.*

Have you ever observed closely a piece of granite? It has three distinct substances mixed together: small black specks, which are particles of *mica*; small white crystals which are *quartz*; and a grayish substance called *feldspar*. Each of these (*mica*, *quartz*, and *feldspar*) is a compound. Every molecule in every piece of *mica* is a *mica* molecule, and different from every other kind of molecule in the world. Every molecule in every bit of the *quartz* is a *quartz* molecule, composed of one atom of silicon and two atoms of oxygen. The molecules in the *feldspar* are all alike, but they differ from all other kinds of molecules. Granite must, therefore, be a mixture, because it contains three kinds of molecules.

Mixtures may vary in composition. Besides containing different kinds of molecules, no two pieces of granite are exactly alike. Some have larger pieces or more pieces of *mica* in them

than others, and some may contain more quartz or feldspar. If you were to pick up twenty pieces of granite in twenty different places, you would have twenty different kinds of granite. If, however, you were to gather twenty pure samples of a compound like water from as many places, even if one sample came from the North Pole, one from Antarctica, and one from the Equator, all would be exactly the same. The molecules would all be those of water, and every molecule in each of the samples would consist of two hydrogen atoms clinging to one oxygen atom. The formula for water is H_2O . A formula shows the elements and the number of atoms of each element that are held together in a molecule of a compound.

A mixture can be divided into its components by physical means. If we were to crush a piece of granite, we could easily pick out the pieces of mica from the remainder of the rock. A river causes this separation of the three substances as it flows over granite boulders. The mica particles, being light in weight, float along in the water or are deposited on top of the sand, where they may glisten like flakes of gold. The quartz crystals become river sand, and the feldspar forms deposits of clay.

If we take a cupful of sand and one of sugar, and shake the two together thoroughly, we have a mixture, because there are at least two kinds of molecules. The sand crystals are composed of silicon dioxide molecules, while the sugar crystals contain only sugar molecules. We might separate the sugar crystals from the sand crystals by picking them out with the aid of a magnifying glass and a pair of tweezers, but it would be a laborious process. It would be far easier to pour the mixture into water, in which the sugar readily dissolves and the sand fails to dissolve. If we allowed the sand to settle to the bottom, we could pour off the solution of sugar and water, dry the sand, and again obtain our cupful of sand. The sugar could be recovered from the solution by evaporating the water under reduced pressure. If we evaporate the water from a sugar solution under ordinary conditions, the sugar darkens and changes to caramel before all the water from the solution is removed. The temperature of the boiling solution is high enough to decompose some of the sugar molecules. If we were to continue the heating, nothing but a residue of carbon would remain in the container. If, however, the solution is boiled under reduced pressure, the water from the solution passes off at a temperature below that at which the sugar itself is decomposed. We might also separate the mixture of sand and sugar by placing in it insects that eat sugar. The insects would remove the sugar crystals and leave the sand crystals unchanged.

We have already stated that two pieces of granite from different localities or from two different boulders rarely have the same amounts of mica, quartz, and feldspar in them. Likewise, no two mixtures of sand and sugar need be alike. Instead of mixing the sugar and sand in equal amounts as suggested above, we might use one-half of a cup of sand to one cup of sugar, or 10 cups of sand to one cup of sugar. In other words, many different mixtures of the same two or more substances can be made.

We might understand a mixture more fully by examining the result of shaking together a lot of peas and beans. No matter how thoroughly you shake and stir them, the two components (peas and beans) remain unchanged. You can easily pick out the peas and beans from the mixture and place them in separate piles. There is a very slight chance that two mixtures of peas and beans would contain the same number of each of these components. One mixture might contain 100 peas and 300 beans; another, 200 peas and 200 beans, and so on.

Compounds are constant in composition. Every molecule of water contains 2 hydrogen atoms and 1 oxygen atom; every molecule of ordinary sugar contains 12 carbon atoms, 22 hydrogen atoms, and 11 oxygen atoms. (Its formula is $C_{12}H_{22}O_{11}$.) Every sodium chloride ($NaCl$) molecule contains one sodium atom and one chlorine atom. *A compound always has the same composition.* Moreover, molecules of compounds cannot be separated into their atoms by physical means. We cannot separate a sugar molecule into its atoms by dissolving some of the atoms and leaving other atoms undissolved; the molecule of sugar dissolves as a whole. Likewise, if we grind a sample of sugar, no matter how thoroughly, we find that the substance still exists in the form of molecules, and that we have not separated the atoms that make the molecule. Fish are as dependent upon oxygen as we are, and they cannot live in water that does not have air dissolved in it. Water itself contains plenty of oxygen (eight-ninths by weight), but this oxygen is not in the free state. It is combined with hydrogen, and the fish cannot decompose the water molecules and inhale the oxygen. Some free oxygen from the air dissolves in water, and fish are dependent upon this *dissolved* oxygen for their breathing. Compounds cannot be separated into their elements by physical means, as can mixtures. The separation is accomplished by chemical means only.

Questions and Exercises

1. What is an element? What is a compound?
2. Name an element in which the atoms exist singly.

3. Name an element in which the atoms exist in pairs.
4. Why cannot an element be decomposed into different kinds of matter while a compound can?
5. What difference exists between a molecule of an element and a molecule of a compound?
6. How many elements are known?
7. What is meant by the statement that an element exists in the *free state*?
8. What is meant by the statement that an element exists in the *combined state*?
9. How does a mixture differ from a compound?
10. Which of the following do you believe to be pure substances, and which mixtures: (a) sugar, (b) coffee, (c) distilled water, (d) soil, (e) milk, (f) sulfur, (g) copper, (h) cement, (i) granite?
11. Which of the following are elements and which are compounds: (a) water, (b) oxygen, (c) salt, (d) iron, (e) copper?
12. Which of the following substances are composed of molecules that are all alike: (a) sugar, (b) milk, (c) salt, (d) alcohol, (e) wheat, (f) water?
13. Which of the following substances are composed of atoms that are all alike: (a) gold, (b) bread, (c) sulfur, (d) paint, (e) iodine?
14. Why are earth, air, fire, and water no longer considered to be elements? Is any one of these a compound; a mixture?
15. Which is the most abundant of the elements?
16. Can you name any elements other than those mentioned in this chapter?
17. Can you suggest why the element oxygen was not discovered until near the end of the eighteenth century?
18. What is the "symbol" of an element?
19. How are symbols chosen?
20. Name five mixtures and tell how you could separate the components.
21. Can you tell from the appearance of a compound the elements of which it is composed?
22. Can you tell by the appearance of a mixture the elements of which it is composed?
23. Can you think of a reason for the fact that gold and copper were known for many centuries before aluminum was discovered, although the latter is far more abundant?

PART 3

Physical States of Matter; Crystals

Matter exists in three physical states. From the earliest times substances have been classified as gases, liquids, and solids. When we describe a substance, we usually mention its physical state, that is, whether it is a gas, a liquid, or a solid. We have said that air is a mixture of gases, that water is a liquid, that iron and sugar are solids. We mean that air is a gas at the ordinary temperatures of our atmosphere. Air can be liquefied, and it can also be changed to a solid, but only at extremely low temperatures. A substance like water which we should ordinarily class as a liquid might be called a solid by a person living at the North or South Pole. We have seen also that water exists in our atmosphere in the gaseous state. However, the greatest amount of water on the earth is in the form of a liquid, hence we usually call it a liquid. All gases can be liquefied. All liquids can be changed to solids and most liquids can be converted into gases. Not all solids can be changed to the liquid and gaseous states. If we heat solid water (ice), it melts easily at $0^{\circ}\text{C}.$, forming liquid water. If the heating is continued, the water becomes warm, then hot, and finally boils at $100^{\circ}\text{C}.$, where it changes rapidly to water vapor, which is gaseous water. Conversely, if gaseous water is cooled, it returns to the liquid state. On continued cooling the water reaches its freezing point, the liquid disappears, and only solid water (ice) remains.

On the other hand, if we were to heat a solid like flour, it would not melt and form liquid flour. Flour decomposes when heated, forming water, charcoal, and other products. The decomposition products have no resemblance to flour—they are entirely different substances. Just why do these different states of matter exist? Since all matter is composed of molecules, there must be some difference in the behavior of the molecules in gases, liquids, and solids.

Gases. In gases the molecules are relatively far apart. They are so far distant from one another, compared with the size of the molecules themselves, that the attractive force between them, called *cohesion*, is negligible. Each molecule flies about inde-

pendently, until it collides with another molecule, or the walls of the containing vessels. Then it is deflected into a different course, in which it continues until another collision occurs. The average velocity of the gas molecules of the air at ordinary temperatures is about 20 miles a minute, and each molecule suffers about 250,000 collisions in going an inch.

We can easily prove that the molecules of a gas are in motion by opening a bottle of ammonia gas for a moment, in a closed room. The odor of the gas may soon be detected in all parts of the room. In a comparatively short time the molecules of ammonia are evenly distributed throughout the room; that is, if we were able to count these molecules, we should find the same number in every cubic foot of air contained in the room. They have separated from each other by distances many times greater than the distances between them when they were in the original bottle. A gas has no definite size or shape, but distributes itself uniformly throughout the container.

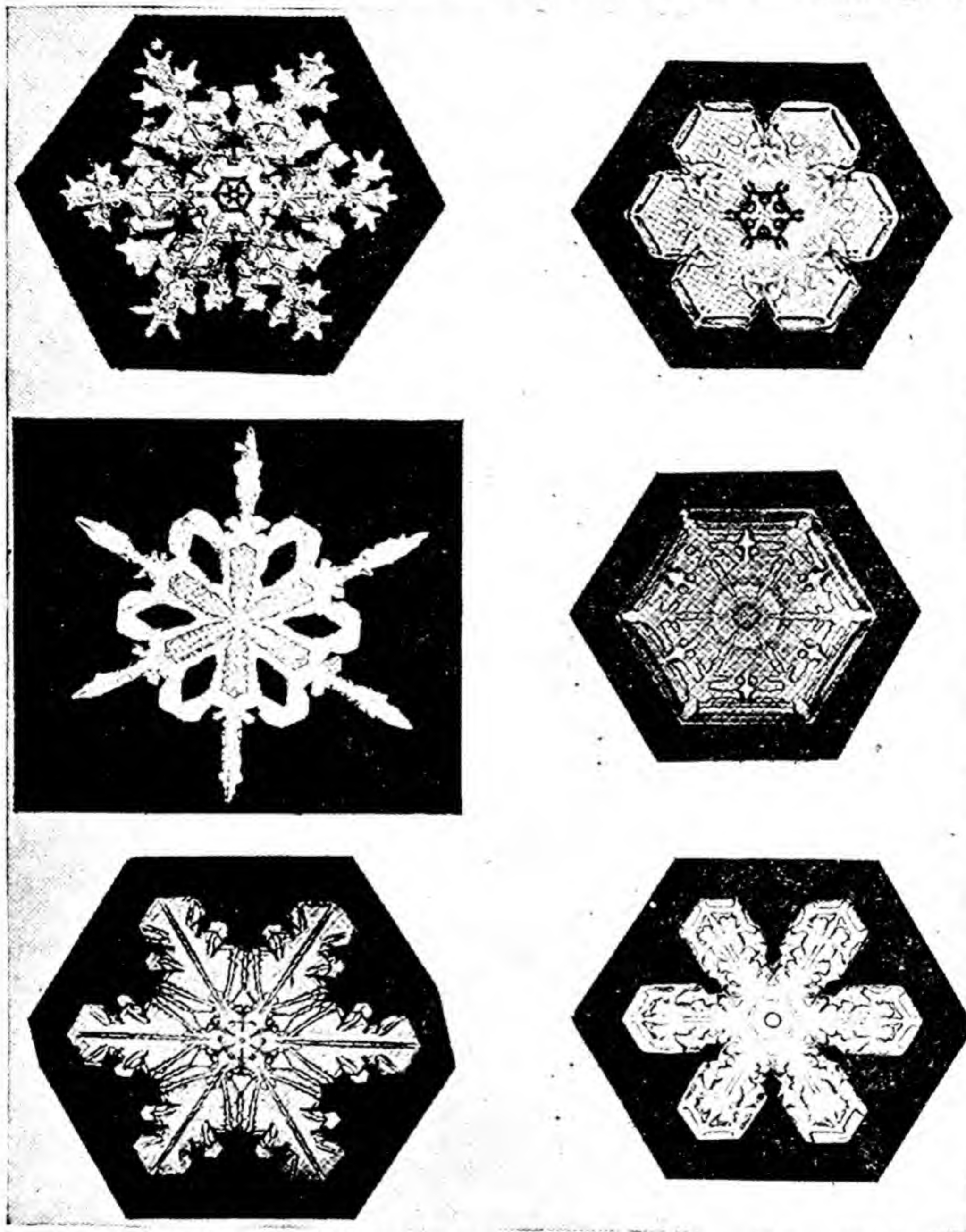
It is impossible for us to form a mental picture of the number of molecules in what we commonly consider a small quantity of matter. The population of the world is approximately two billions, and if every man, woman, and child should count at the rate of four per second, and continue counting day and night without interruption, it would require approximately 100,000 years to make the total count equal the number of molecules in one quart of air. The number is approximately 24,000,000,000,000,000,000,000.

When a molecule strikes the wall of the containing vessel, it exerts a push, and the result of a great many of these blows on the wall produces the effect of a steady pressure. Molecules of gases move more swiftly at higher temperatures; hence, as the temperature is increased, the molecules strike the wall harder and more frequently. The pressure exerted by a gas, therefore, increases as the temperature is increased, and decreases as the temperature is lowered. For this reason the pressure in an automobile tire becomes greater on a hot day. Rapid driving also overheats a tire, through friction, and this overheating may cause a gas pressure too great for a weak tire, the consequence of which is a blowout.

When more molecules are crowded into a given space, the number, of collisions per minute with the walls of the container is increased causing an increase in pressure. We are careful not to overinflate an automobile tire lest we cause a blowout in this manner.

Liquids. In liquids the molecules are much closer together than they are in the gaseous state. There is considerable cohesive

force acting between the molecules. Even so, the molecules are free to wander and exchange positions; hence, liquids have no independent shape, but assume the form of the containing vessel.



From Bentley and Humphreys, "Snow Crystals." Courtesy, McGraw-Hill Book Co.

Fig. 11. Water crystallizes with hexagonal symmetry.

If a liquid is heated, the molecules move faster and faster, exactly as in the case of a gas. They are driven farther and farther apart until, finally, those on the surface escape and become gas molecules. As a liquid is cooled, the molecules move more and more slowly and get closer and closer together until, finally, they form a solid at the so-called freezing point of the liquid.

Solids. In the solid state the molecules are held closely together and are unable to move about freely because of the tremendous attractive force existing between the molecules. Since each molecule occupies a definite position, solid matter has a definite shape which is not easily changed. In a rod of iron 1 sq. in. in cross section, the cohesion is so great that it requires a force of many tons to pull the iron molecules apart. Similarly, it takes a large amount of heat to tear the molecules apart and allow them to move as freely as they do in a liquid, but at a high temperature iron can be melted and made to flow like water.

Crystal forms. When a solid is formed by cooling a liquid to its freezing point, or when it is formed by the evaporation of the liquid from a solution of the substance, the solid mass is usually found to be composed of particles of regular geometric form, called crystals. When crystals of sodium chloride are formed by allowing a hot, saturated solution of salt to cool gradually to room temperature, many of the crystals are found to be perfect cubes. Sodium chloride always crystallizes in the form of cubes.

Many substances form crystals characterized by definite angles between the faces. The shape of the crystal of any substance is as much a property of the substance as is its melting point, its density, or its color. The determination of the crystal form of a substance is an aid in its identification. A well-trained mineralogist can identify a piece of rock or ore merely by observing the kind of crystal or crystals of which it is composed. Crystal forms are usually classified, for convenience, into six different systems:

(1) *Regular, or cubic system.* Three axes of equal length at right angles to each other. This system includes the cube,

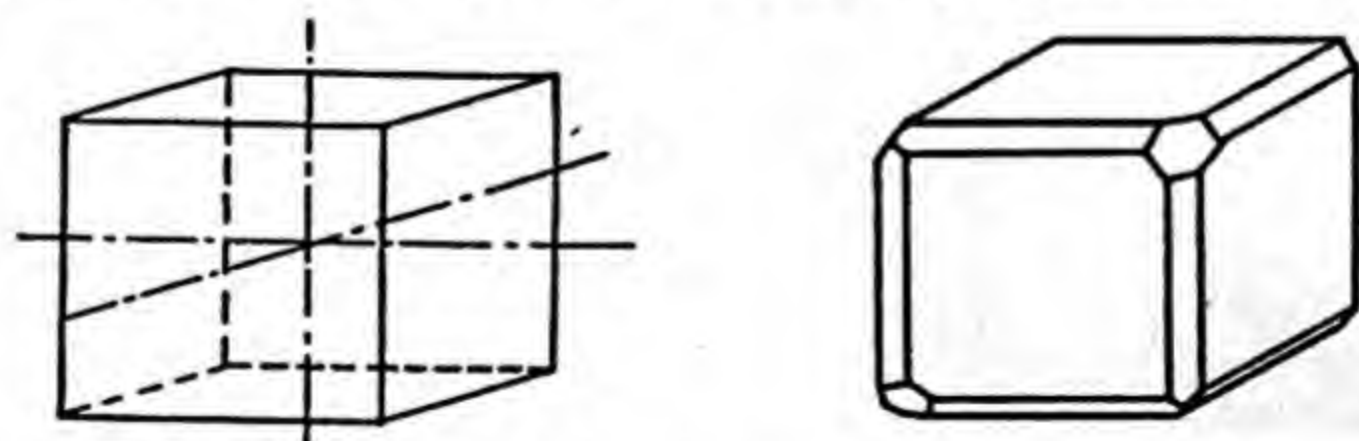


Fig. 12. Cubic system.

in which form sodium chloride and fluorspar crystallize; the octahedron, in which alums crystallize; the dodecahedron, which is represented by the garnet.

(2) *Tetragonal system.* Two equal axes and one axis either longer or shorter than the other two, all at right angles to each other. Typical forms of this system are prisms and pyramids.

Nickel sulfate, tin oxide (cassiterite), and potassium ferrocyanide crystallize according to this pattern.

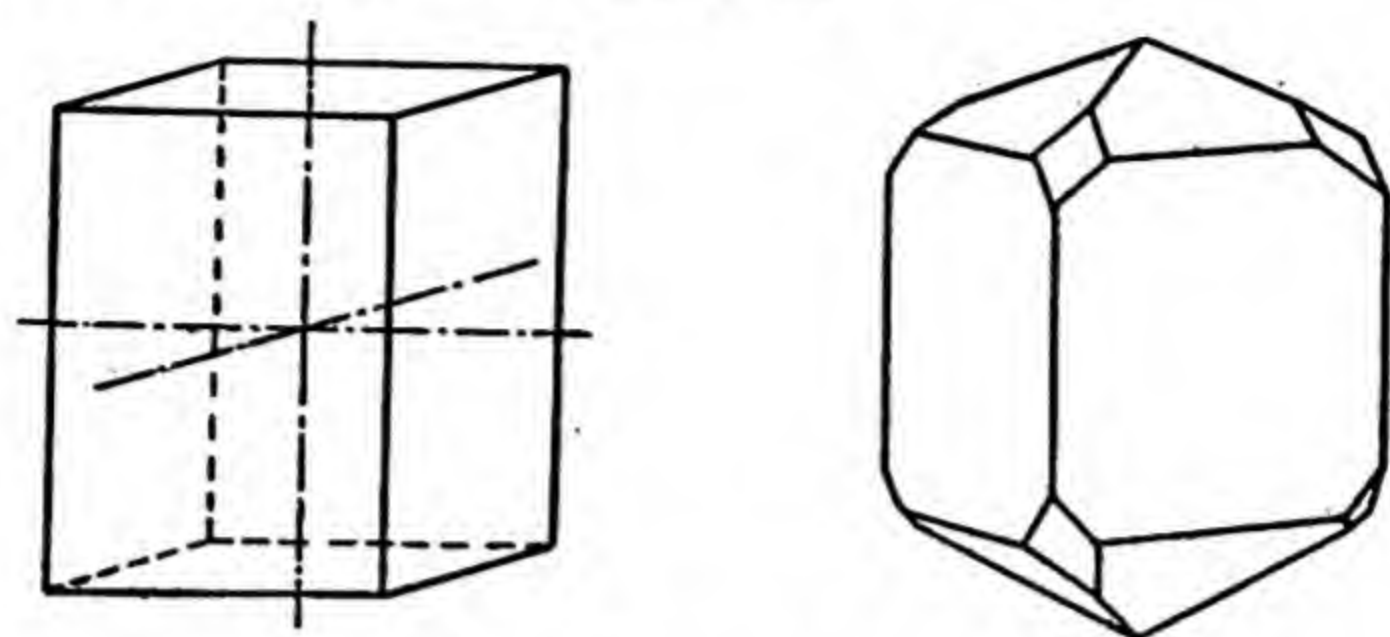


Fig. 13. Tetragonal system.

(3) *Rhombic system*. Three unequal axes all at right angles to each other. Sulfur, zinc sulfate, aragonite (calcium carbonate),

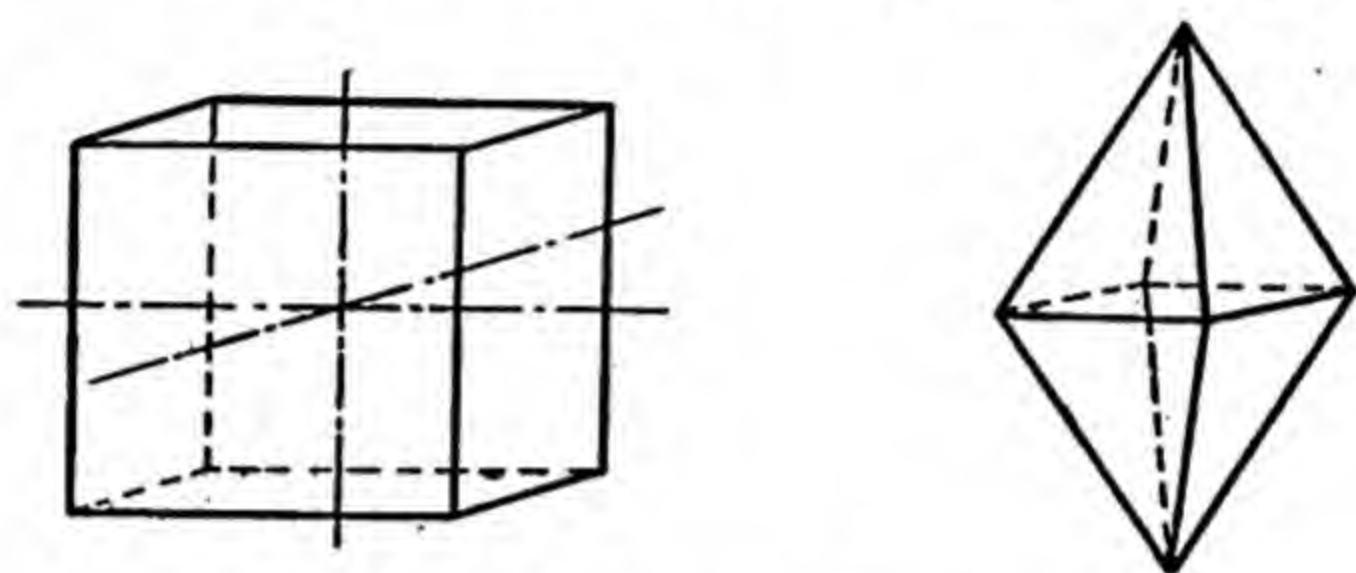


Fig. 14. Rhombic system.

magnesium sulfate, and potassium nitrate form crystals in this system.

(4) *Hexagonal system*. Three equal axes in the same plane, intersecting at angles of 60° , and a fourth axis through the intersection and perpendicular to the plane. The minerals witherite

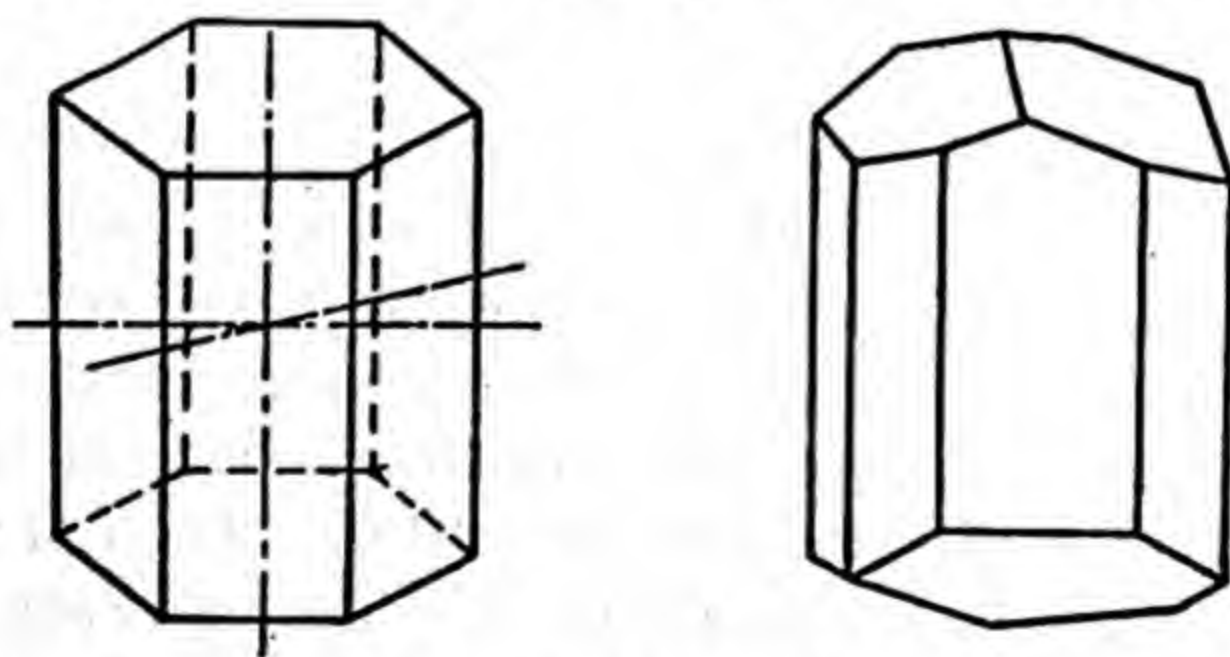


Fig. 15. Hexagonal system.

(barium carbonate), beryl (beryllium aluminum sulfate), and apatite (calcium fluoride-calcium phosphate) form crystals in this system.

(5) *Monoclinic system*. Three axes of unequal length, two of which intersect at an oblique angle, while the third is perpendicular

to the plane of the other two. The oblique angle of intersection of the first two axes may vary from 0° to 90° . Examples of crystals

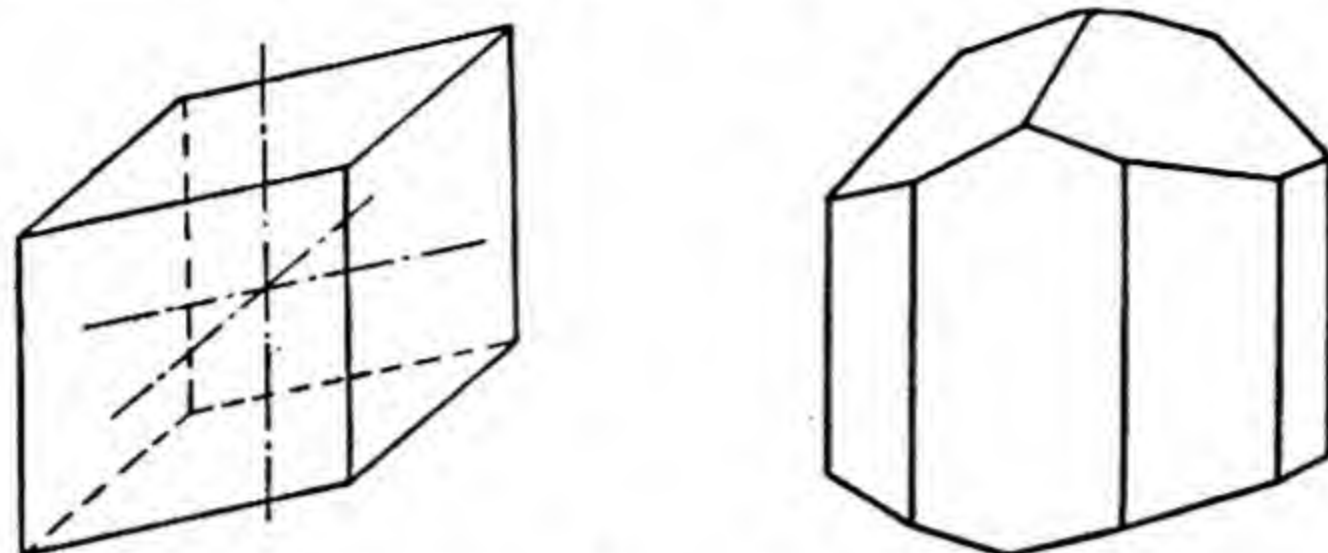


Fig. 16. Monoclinic system.

belonging to this system are gypsum, borax, sodium carbonate, and rock candy.

(6) *Triclinic system*. Three unequal axes, all of which meet at oblique angles. Potassium dichromate and copper sulfate crystallize in this manner.

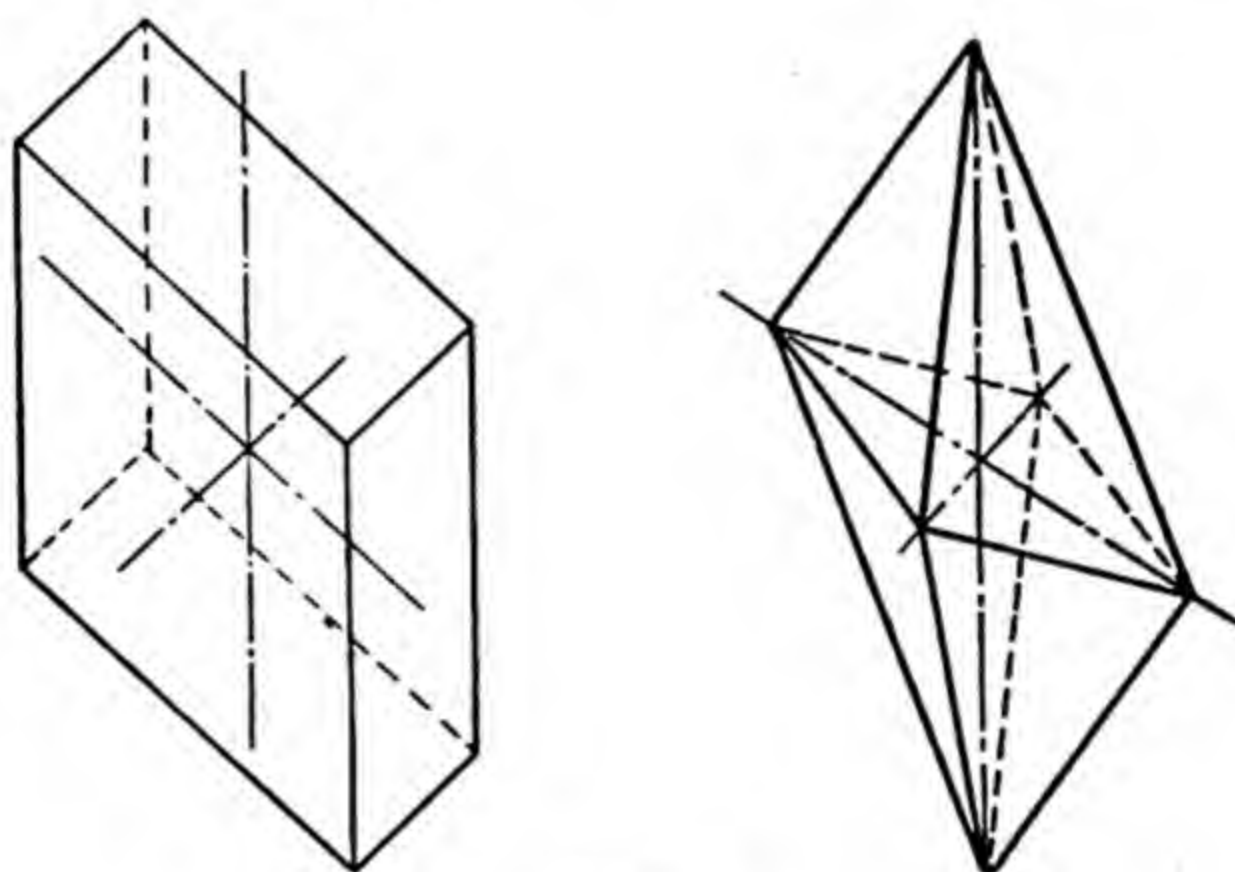


Fig. 17. Triclinic system.

Crystal structure. Since a substance crystallizes in a definite form, it is evident that the particles—atoms, ions, or molecules—of which the crystalline solid is composed must always be arranged in the same order. Such a definite arrangement of the particles is called a *crystal lattice*, or a *space lattice*. The lattices in any two crystals of the same substance are alike. In a large crystal the basic crystal lattice of the smaller crystal is merely repeated.

Most of the particles of which the crystal is made lie in planes which are parallel to the faces of the crystal, while the spaces between these planes contain few or no particles. The distances between these particle-rich planes is about equal to the wave length of ordinary X rays. When a beam of X rays is directed onto a crystal, some of the rays pass directly through the crystal in the spaces between the particles, but when this extremely short

form of light wave strikes a particle, the particle becomes a center of radiation, reflecting the wave which strikes it. When the many particles in a plane in the crystal reflect the waves which strike them, they may reflect enough of the radiation to affect a photographic plate placed near the crystal in the line of the reflected waves. If the distances between these planes in the crystal bear such a relationship to the length of the X ray striking them that the waves from deeper layers join (in the same phase) those which are reflected from the plane of particles in the face of the crystal, then a definite pattern is observed on the photographic plate.

This method of measurement has been employed in the laboratory to determine the distance between the planes of particles in a crystal. A beam of X rays of known wave length is directed onto a crystal at an angle which causes reinforcement of the energy from the planes of atoms parallel with the face of the crystal. The distance between the planes may then be calculated. The crystal is then turned, and the distance between the planes of particles parallel to another face of the crystal is determined in the same manner.

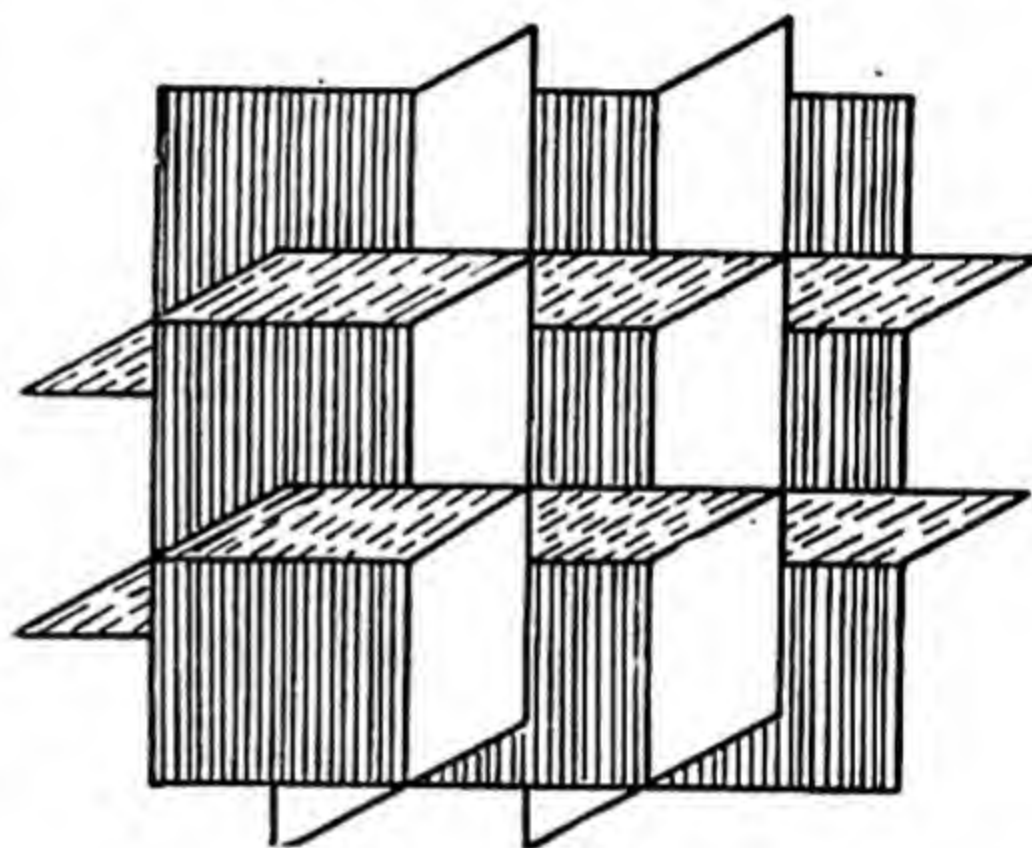


Fig. 18. The atoms in the crystal lattice are located at the points of intersection of the planes.

The particles of which the crystal lattice is built are located at the points of intersection of all the particle-rich planes. For example, suppose we allow a beam of X rays to fall upon a face of a crystal of sodium chloride, at such an angle that the plate shows reinforcement of the waves from the particles in the planes parallel to this face. From the measured angle and the known wave length, the distance between these planes can be calculated. If the process is repeated for each of the other pairs of parallel sides of the cube, the distances between the planes parallel to these sides may also be determined. Since all these planes (at right angles to each other in this case) contain the atoms (or ions) of which the crystal is composed, it follows that the points at which the three sets of planes intersect will be occupied by the particles, as shown in Fig. 18.

The arrangement of sodium atoms and chlorine atoms in a crystal of common salt is shown in Fig. 19. Each interior sodium atom is surrounded by six chlorine atoms equally distant from it

and from each other.

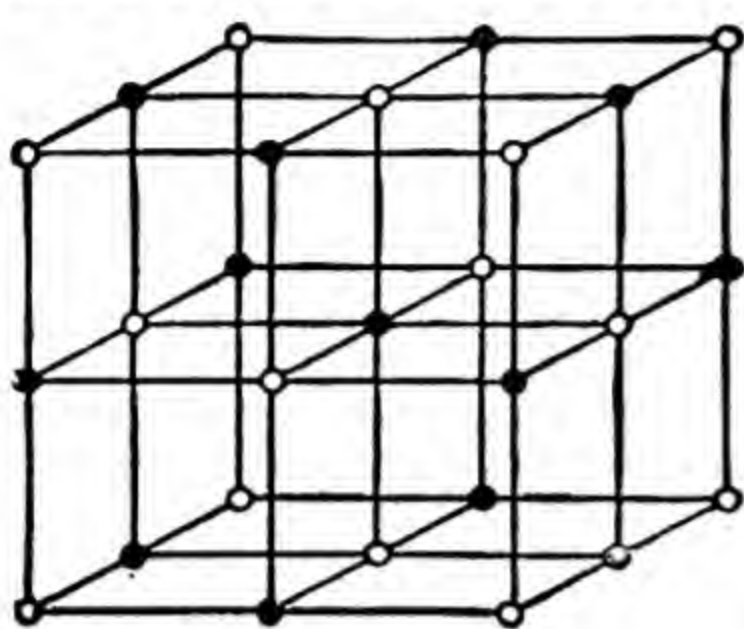


Fig. 19. The crystal lattice of sodium chloride. The black circles represent sodium atoms and the open circles chlorine atoms.

ordered arrangement. Such a solid is said to be *amorphous*, which means "without form."

Similarly each chlorine atom is surrounded by six sodium atoms. We cannot correctly say that any particular sodium atom is combined with any single chlorine atom in the crystal, but since sodium and chlorine atoms are present in equal numbers in the crystal, we may still consider that the simplest unit of sodium chloride is the molecule. NaCl, as it actually exists in the gaseous state.

Amorphous solids. Some solid substances, such as clay, do not form crystals of any kind. The particles are massed together in lumps in which there is no

Questions and Exercises

1. A bottle of perfume is opened for a moment, then closed. A few minutes later the odor of the perfume can be detected in any part of the room. Explain.
2. Why does the pressure in an automobile tire increase when the car is driven at high speed?
3. Compare the melting points of iron and lead. In which of these metals do you think the molecules are more firmly held together?
4. Is it possible to change a solid substance to a liquid without changing its composition? Does this answer apply to all solids?
5. Name two solid substances that cannot be vaporized on account of their tendency to decompose when heated.
6. Give evidence that the air molecules in the atmosphere are not closely packed together.
7. Are there any gases that cannot be liquefied?
8. How do the arrangements of the molecules differ in solids, liquids, and gases?
9. How do gas molecules produce a pressure?
10. Why does the pressure of a gas in a sealed vessel increase when the gas is heated?

PART 4

Properties of Matter and Energy: Chemical and Physical Changes

Physical properties. When we hear the name "copper," a definite picture of the element comes to our minds. We may visualize a copper coin, a copper wire, or some other object which we have seen that is made of this metal. We recognize copper by its color. This quality, color, which helps us to distinguish copper from all other metals, is called a *property* of the metal.

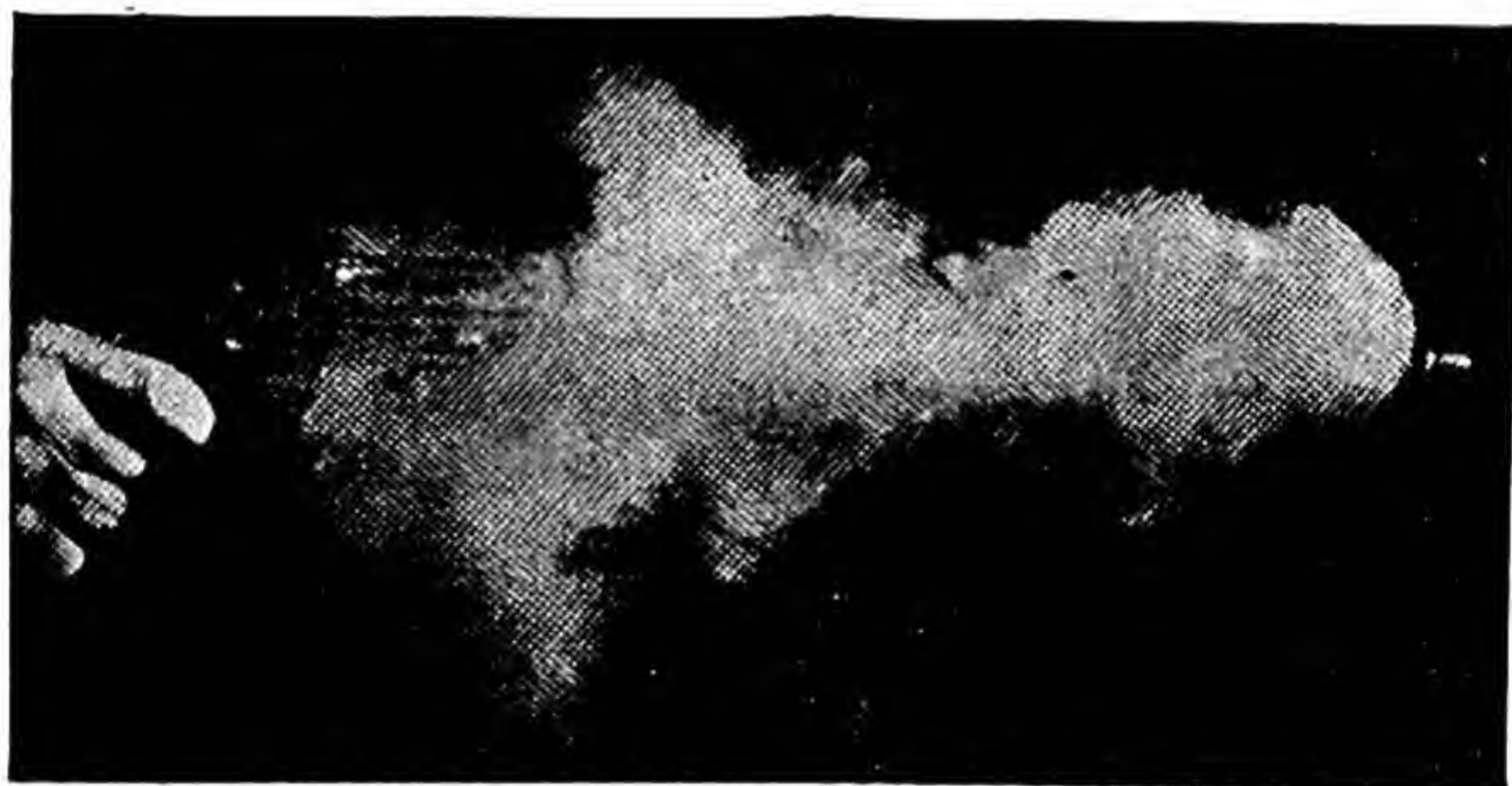


Photo by Harold E. Edgerton, Massachusetts Institute of Technology

Fig. 20. The powder has undergone a chemical change. A physical change has been imposed upon the bullet. Exposure, one millionth of a second.

Again, the word "water" brings to mind a substance with definite properties. We may think of it as a liquid which is odorless and almost tasteless. We may visualize a lake, colorless near the shore but becoming blue in the deeper parts, or we may think of a steaming kettle of water on a hot stove. Water boils at a definite temperature, which is 100°C . (see page 17). At this *boiling point* the liquid water is changed to water vapor, or, as we ordinarily say, to steam. When the temperature falls to 0°C ., its *freezing point*, water changes from the liquid to the solid state, ice. These characteristics are properties of the substance water.

The substance iron is easily distinguished by its properties. It has a gray color, it is hard, and it conducts heat readily. An iron poker soon becomes too hot to be handled with comfort when used to shift the burning logs in a fireplace. Pure iron is malleable; that is, it can be hammered into various shapes.

Some of the properties of silver are well known to all of us—its white color, its luster, its density, and its relative hardness. It conducts electricity more easily than any other metal, and it is ductile; that is, it can be drawn out into fine wire.

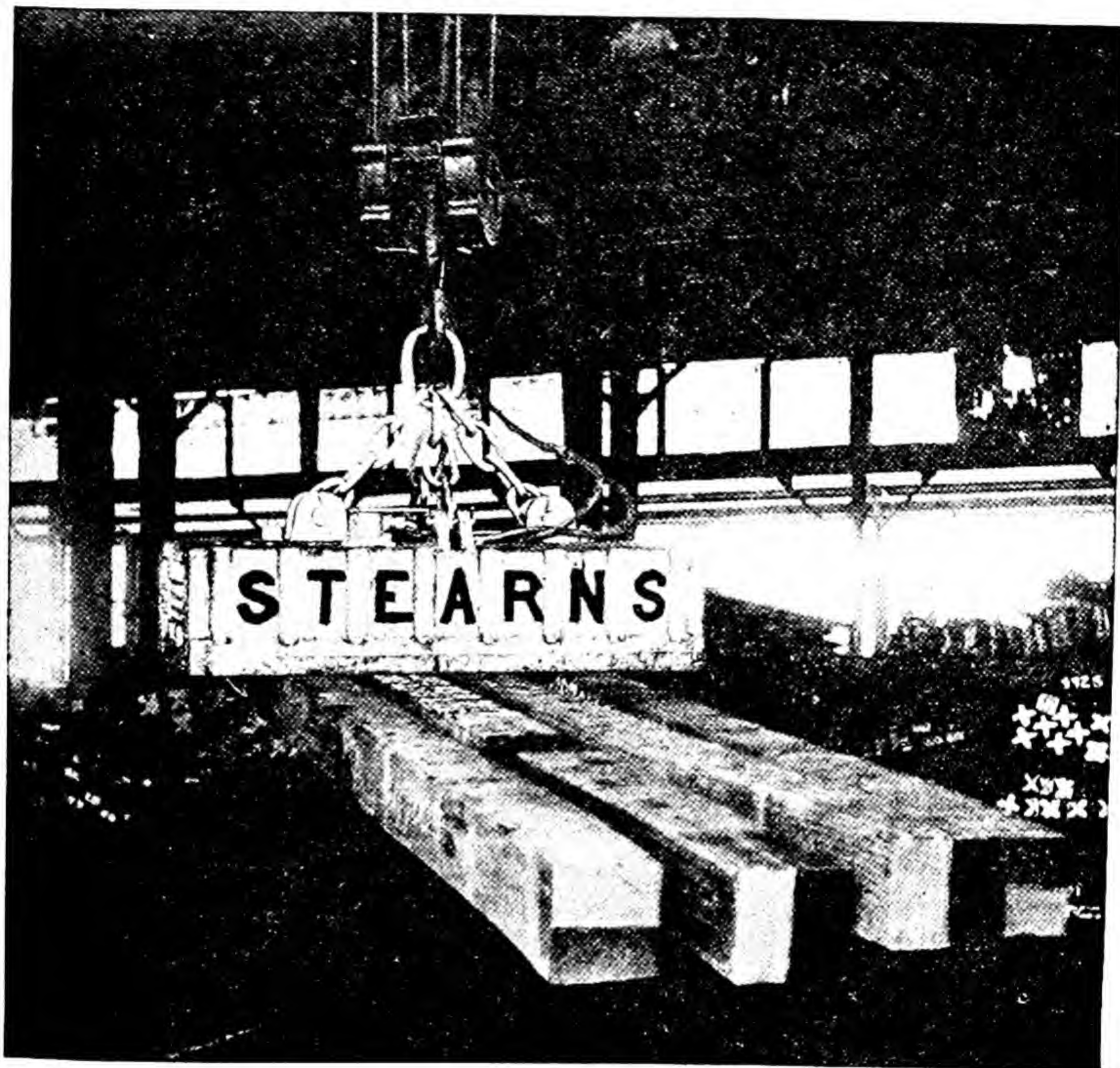
Color, taste, odor, physical state (gas, liquid, or solid), boiling point, freezing point, conductivity for heat, malleability, hardness, density, conductivity for electricity, and ductility are all *physical properties*. They are properties that can be observed without changing the substance into some new kind of matter.

Chemical change. We have said that the metal sodium combines with the gas chlorine to form sodium chloride. The tendency that sodium has to combine with chlorine is called a *chemical property*. Wood, kerosene, and gasoline burn. The fact that these substances will burn, when given an opportunity to do so, is called a chemical property. The actual burning of a substance is an example of a *chemical change*, or a *chemical reaction*. When a chemical reaction takes place, the substances taking part in the reaction undergo changes so complete that the original substances can no longer be recognized in the final products. When sodium combines with chlorine, a chemical change takes place in which a product entirely different from the original elements is formed. Some metals dissolve in acids, setting free the gas hydrogen, and leaving a substance very different from either the metal or the acid. A chemical reaction has taken place.

When a piece of iron is thrown into a wet, swampy place and is allowed to remain there for some time, it becomes covered with a reddish-yellow, earthy substance which has none of the properties of the original iron. This new substance does not have a metallic appearance, it will crumble readily if struck with a hammer, and it is not attracted by a magnet. It is heavier than the iron from which it was formed. Rust is a compound of iron and oxygen, and each molecule of rust contains two atoms of iron and three of oxygen. The compound does not resemble either of the elements of which it is composed; accordingly, the formation of rust from iron and oxygen is a chemical change.

The souring of milk is another familiar chemical change. The lactic acid liberated imparts a taste very different from that of the original milk.

In all these illustrations of chemical change, the materials with which we started are changed into others of entirely different composition, and hence, into materials having entirely different physical and chemical properties. A chemical change may be defined as a *change in the composition of matter*.



Courtesy, Stearns Magnetic Mfg. Co.

Fig. 21. An electromagnet lifts many tons of steel.

Physical change. A change in the properties of a substance which is not accompanied by the formation of a new kind of matter is called a physical change. When water is boiled and changed to steam, the substance is still composed of water molecules. Likewise, when water is frozen to ice, the molecules are all water molecules, as they were in the liquid state. Only a physical change has taken place, for no new kind of matter has been formed. Liquid water and ice represent different physical states of the same compound.

A piece of soft iron becomes a magnet when it is placed within a coil of wire through which an electric current is flowing. When the current ceases to flow through the wire, the iron loses its magnetic properties. The magnetization of soft iron is a physical change.

When a piece of platinum wire or the tungsten filament in an electric light bulb has become heated so that it glows and gives out light, a physical change has taken place. The substance out of which the wire or filament was made has not changed, and it will return to its original condition on cooling.

Conservation of matter. We have said that when a chemical change or reaction occurs, the products are entirely different from the substances with which we started. One thing, however, holds true for all such changes: *Matter is neither created nor destroyed during a chemical reaction.** If we weigh a sample of sodium chloride, we find that its weight is the sum of the weights of the sodium metal and the chlorine gas which have gone together to form the sodium chloride.

When acid is poured onto a metal like magnesium, the substance remaining in the container at the end of the reaction actually weighs less than the sum of the weights of the magnesium and the acid. If, however, we catch and weigh the hydrogen gas which is evolved during the reaction, once again our weights before and after the reaction exactly balance.

When kerosene burns, nothing remains behind. It might seem that matter is destroyed in this process, but a chemist knows that the products of the combustion are two invisible gases, carbon dioxide and water vapor. If these gases were caught and weighed, their weights together would be greater than that of the kerosene which was burned. This increase would seem to prove that, during the process of burning, matter is actually created. If, however, we should weigh the oxygen gas that is taken from the air and used during the burning, we should again find no increase or decrease in the total weights of the substances.

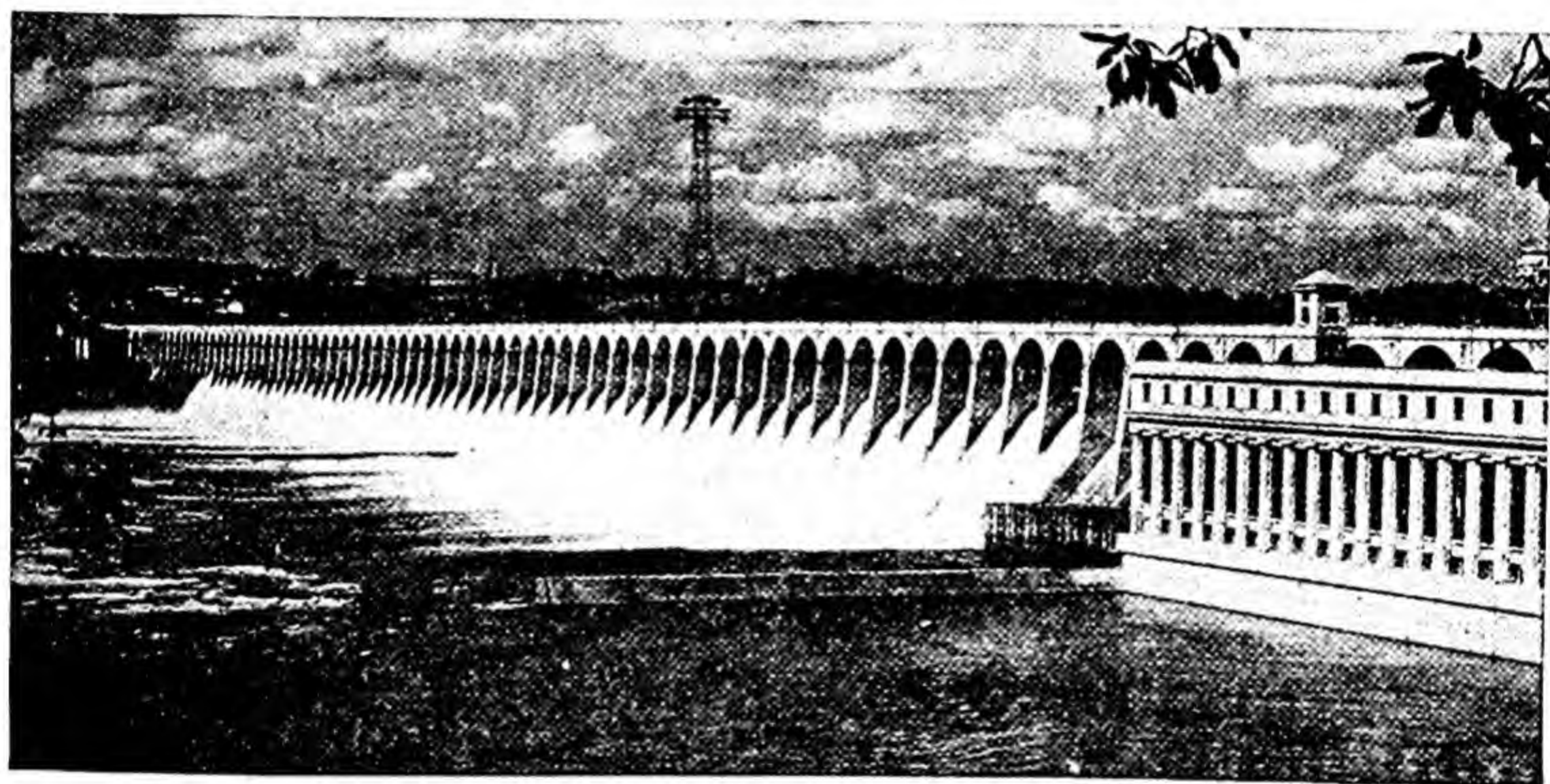
Iron rust weighs more than the iron from which it was made. The difference in weight is equal to the weight of oxygen taken from the air during the rusting process.

Painstaking chemical work shows that, if all the substances concerned in a chemical change are weighed before and after the change, there is no weighable alteration in the quantity of matter.

* Actually, the escape or absorption of heat or the loss or gain of energy in any other form results in a corresponding loss or gain in matter, but the change in weight due to a chemical reaction is too small to be detected by the use of an analytical balance.

We say, therefore, that *matter cannot be created or destroyed*. This is known as the law of the conservation of matter.

Conservation of energy. We should not think of the physical and chemical changes taking place in matter without considering the energy changes which are always associated with them. Anything that can do work possesses energy. When a large body of rock and earth becomes dislodged from the side of a mountain, it can demolish houses in its downward path because of the tremendous amount of energy it possesses. A river, swollen by rains or melted snow, can tear bridges from their foundations



Courtesy, Tennessee Valley Authority

Fig. 22. The energy of running water is converted into electrical energy.

because of its kinetic energy, or energy of motion. A wound clock spring possesses energy and does the work necessary to keep the clock running. A small charge of dynamite can move tons of earth because of the chemical energy in the dynamite. Every chemical reaction either liberates or absorbs energy while the reaction is taking place. Usually the energy is liberated or absorbed in the form of heat. When heat is given out, we say that the reaction is *exothermic*; when heat is absorbed, the reaction is said to be *endothermic*.

As in the case of matter, we can neither create nor destroy energy. One form of energy can be transformed into another, but the quantity of energy is not changed in any process.

The energy possessed by a rapidly flowing river or waterfall can be converted into electrical energy by placing an electric generator in its course. The electrical energy is carried by wires from the generator into our homes, where it may be converted

into heat energy in our waffle irons, hot plates, and electric stoves. Electrical energy is converted into heat and light energy in an electric bulb. The chemical energy which is released as heat when coal or oil burns may be used to change water to steam, and the steam may be used for imparting motion to the pistons of a locomotive.

We might mention many other examples of the transformation of energy from one form into another. If we were to measure



Fig. 23. Air in motion carries a useful form of energy.

the energy involved in all these cases, we should find no loss or gain in the total energy involved. Therefore, we conclude that energy may be transformed from one form to another, but energy cannot be created or destroyed. This relation is known as the law of the conservation of energy.*

* It would be more accurate to say that the total amount of matter and energy together in the universe cannot be increased or diminished. It is possible to convert matter into energy and energy into matter, but the loss or gain in matter due to such transformations is very small. It has been estimated that when 20,000,000,000 lb. of coal burn approximately 1 lb. of the fuel is converted into heat and light.

Questions and Exercises

1. How does a chemical change differ from a physical change?
2. Classify the following changes as chemical or physical: (a) the rusting of iron, (b) the effect of boiling an egg (does the egg regain its original properties when cooled?), (c) the addition of water to milk (the water can be removed from the milk by evaporation), (d) the removal of grease from fabrics by gasoline, (e) the burning of wood, (f) the heating of an electric light filament to incandescence by an electric current, (g) the charring of sugar by heat, (h) the ripening of fruit, (i) the boiling of water, (j) an explosion of dynamite.
3. Classify the following as physical or chemical properties: (a) copper conducts electricity, (b) iron rusts in moist air, (c) gold may be rolled into thin sheets, (d) silver tarnishes, (e) water boils at 100°C. , (f) blueprint paper fades in sunlight, (g) milk sours on standing, (h) tungsten melts at 3540°C. , (i) hydrogen burns in air, (j) hydrogen peroxide bleaches hair, (k) magnesium burns in oxygen, forming magnesium oxide, (l) hot magnesium combines with nitrogen gas, forming magnesium nitride.
4. What is the law of conservation of matter?
5. What is the law of conservation of energy?
6. How would you distinguish: (a) gold from copper, (b) coal from slate, (c) starch from talcum powder, (d) sugar from salt, (e) wool from cotton?

UNIT II

The Atmosphere; Oxygen; Hydrogen; Water; Solutions; Gas Laws

PART 1

The Atmosphere

An atmosphere is necessary to life. A planet must have an atmosphere if it is to be inhabited by living forms as we know them. In considering the possibility of life on Mars, scientists have tried to determine whether the planet is surrounded by an atmosphere that can sustain life. Some think it is; others doubt it.

The earth is most fortunate in this respect. It has a rich, extensive layer of air surrounding it. The air supplies us with oxygen for breathing and combustion; it transmits sound; it furnishes us with rain and snow; it reduces the brilliancy of sunlight; and it supplies some of the necessary food for plants, from which we in turn get food, clothing, fuel, and many other useful things.

How high does the earth's atmosphere reach? No one can answer this question definitely. The atmosphere forms a shell around our earth at least 100 miles thick. Airplanes have reached a height of over 10 miles, and balloons carrying recording instruments, but without passengers, have ascended to heights of nearly 20 miles above the earth. At a height of 4 or 5 miles, breathing becomes difficult, for the air becomes less and less dense as the distance from the surface of the earth increases. Aviators take compressed air or oxygen with them when they plan to reach high altitudes. Mountain climbers often have great difficulty in breathing at heights above 10,000 ft. Fortunately there is a supply of air sufficient for all of us at the altitudes in which we live.

Air has weight. Many think of the air as having no weight. We cannot see it, and we can pass through it with ease. However, a bad windstorm or hurricane shows us what it can do when set in motion. It can carry away the soil from the surface of the earth where it strikes, and pile it up in deep drifts in another location, or

keep it whirling through the air for days at a time; it can uproot gigantic trees; it can tear the roofs from buildings and demolish houses. Anyone who has experienced such a storm never doubts again that the air is composed of matter with weight. You can easily prove that air has weight by weighing an automobile tire before and after inflation. A tire which is pumped to its full capacity weighs more than a flat one.

At sea level we find that on every square inch of the earth's surface there is a weight of 14.7 lb. due to air. In other words, a column of air 1 sq. in. in area, extending from the earth to the upper limit of the atmosphere, weighs 14.7 lb. This weight corresponds to more than a ton on every square foot, or 46,100 tons on every acre. Can you figure the weight of air actually resting on you? Assume that the area of your body is 2,000 sq. in. You are not conscious of this weight or crushed by it, because it is balanced by internal pressures.

The barometer. Atmospheric pressure is measured by means of a barometer. The simplest barometer is made by filling a long glass tube with mercury, and inverting the tube in a dish of mercury. The mercury falls, until the weight of mercury in the tube is just equal to the weight of a column of air of equal cross section, extending as high as the atmosphere reaches. The air, pressing on the surface of the mercury in the open dish, holds up the column of mercury inside the tube.

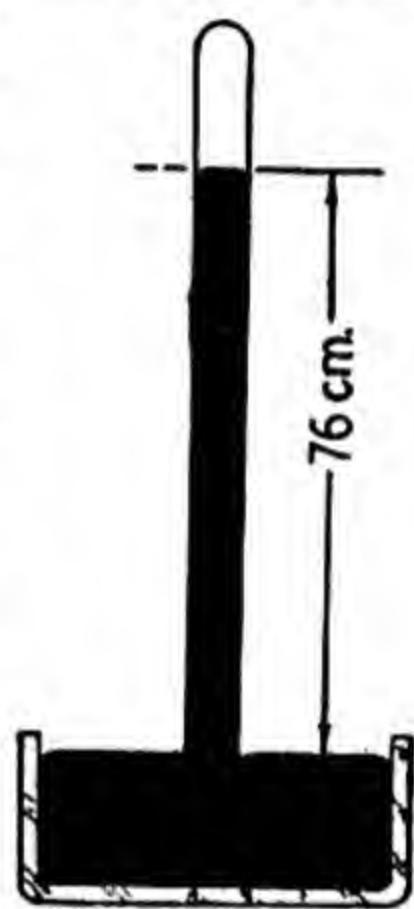


Fig. 24. A simple barometer.

The height of the column of mercury varies with the altitude and with variations in weather. In mountainous regions the column is not so high as it is at sea level. The average height of the mercury at sea level is 76 cm. (760 mm.), or about 30 in. A pressure which will cause a column of mercury to stand 76 cm. high is called "standard pressure." It is often referred to also as a pressure of "1 atmosphere."

Air is a mixture. Air contains molecules of several kinds and, therefore, is a mixture, not a compound or an element. Lavoisier, a famous French chemist, was the first to prove that air is a mixture.

Nitrogen. In 1774 Lavoisier placed some mercury in a retort which was connected by a glass tube to a bell jar filled with air. The bell jar was placed in a trough of water. He heated the mercury for a period of 12 days and found that its surface became coated with an orange-colored powder, much as iron becomes covered with rust. As the orange coating increased in amount, the water rose higher in the bell jar, until it filled one-fifth of the

jar. The powder then stopped forming, and the water rose no higher. Lavoisier reasoned, correctly, that some of the mercury had combined with part of the air to form this orange powder.

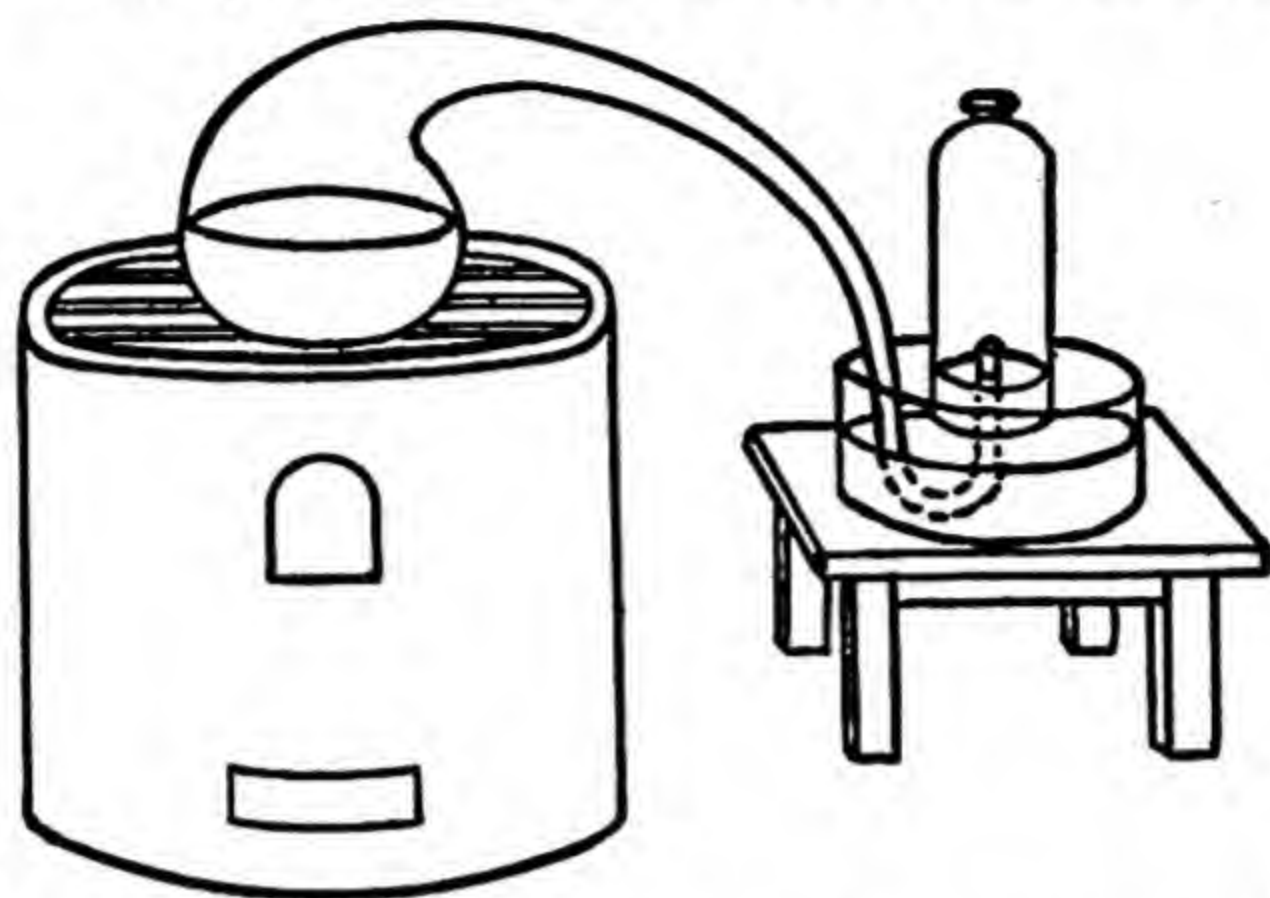


Fig. 25. Lavoisier's experiment with mercury and air.

When animals were introduced into the gas which remained in the bell jar, they died within a few minutes. A lighted candle when placed in the bell jar was extinguished immediately. This gas could support neither life nor the burning of a candle. Lavoisier called the gas *azote*, from the Greek word meaning "without life." English-speaking scientists have named the gas "nitrogen," but the French still use its original name.

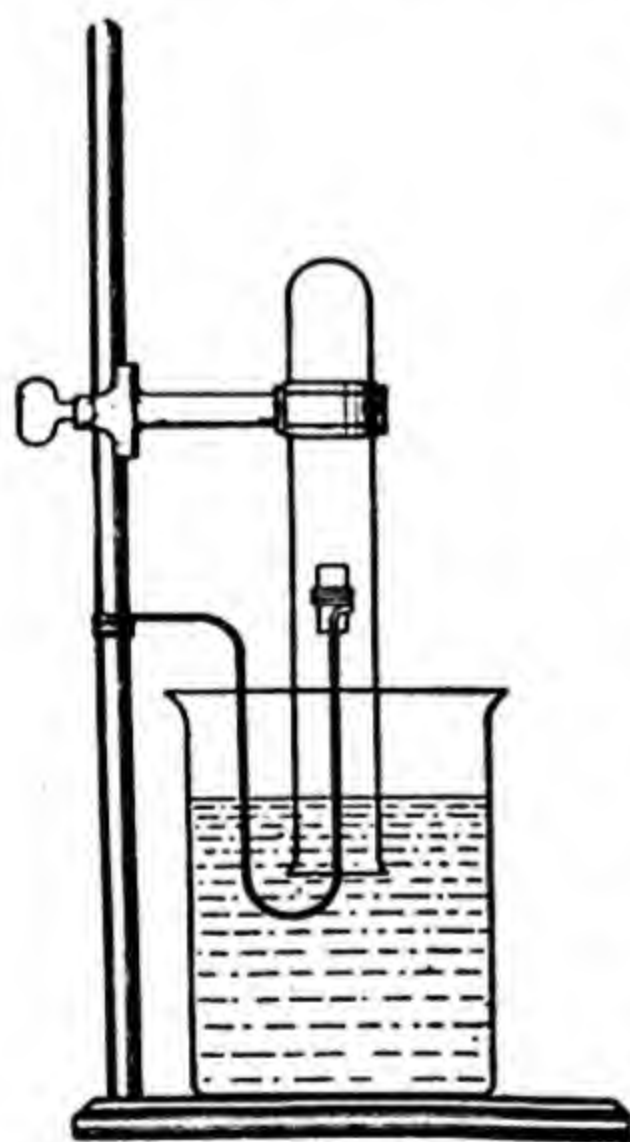


Fig. 26. Removal of oxygen from air by combination with phosphorus.

Oxygen. When the orange powder was strongly heated, it gave off a gas and mercury reappeared. This gas occupied exactly the volume which had been filled by the water when it rose into the bell jar, and hence corresponded in volume with the shrinkage undergone by the enclosed air. The gas also supported life and caused a candle to burn more brightly than in air. Lavoisier, in the mistaken belief that all sour substances contained this element, named it oxygen, from the Greek words meaning "to produce an acid." We now know many acids which contain no oxygen; hence the name is without significance.

Air, then, was shown by Lavoisier to consist of about one-fifth oxygen and four-fifths nitrogen by volume. In the laboratory, by the method shown in Fig. 26, we can prove that air has this composition. A graduated tube is inverted in a trough of water and

a piece of yellow phosphorus, attached to the end of a wire, is placed in the air within the tube. Gradually the oxygen combines with the phosphorus, and we can see a white, heavy smoke dropping from the phosphorus into the water. This is a compound formed from phosphorus and oxygen atoms. As this finely divided white powder dissolves, the water rises in the cylinder until the remaining air occupies only four-fifths of its original volume.

In addition to nitrogen and oxygen, there are several other substances in the air in small amounts. Water vapor is the most abundant of these. The others are argon, carbon dioxide, neon, helium, krypton, and xenon, and traces of other gases. An average sample of *dry air* has the composition shown in the following table.

COMPOSITION OF DRY AIR

Name of gas	Formula	Per cent in air, by volume
Oxygen.....	O ₂	20.98
Nitrogen.....	N ₂	78.04
Argon.....	A	0.94
Carbon dioxide.....	CO ₂	0.035
Neon.....	Ne	0.0012
Helium.....	He	0.0004
Krypton.....	Kr	0.00005
Xenon.....	Xe	0.000006
Hydrogen.....	H ₂	Trace

Water vapor. When water is allowed to stand in an open dish, it gradually disappears. We say that the water has evaporated. Where has it gone? It has changed to gaseous water, single molecules of water, which float off into the air. Gaseous water is called *water vapor*. A certain amount of water vapor is always found in the air, because of evaporation of water from the oceans, lakes, rivers, and from leaves of plants and trees. The actual amount of water vapor that the air can hold at any time depends upon the temperature. On warm days it may be as high as 4 per cent, while on cold days the water-vapor content may be less than 1 per cent of the total volume of the air. When the air holds all that it is possible for it to hold at a given temperature, we say that it is *saturated*. If such air is suddenly cooled, it has more water vapor in it than it can hold at the lower temperature, and the excess appears as fog or a cloud, or it may fall in the form of rain or snow.

When the air is saturated with water vapor, we say that its *humidity* is 100 per cent. During the summer months the air in the Panama Canal Zone usually is saturated. Since human beings

depend largely on the cooling effect of the evaporation of moisture from the surface of the body, they find it very uncomfortable to exercise in localities where the air is already saturated with water vapor. Fortunately for us in most of our communities, the air contains only about half the amount of water which it is able to hold (the average is 66 per cent), so that water evaporates freely from the body and a normal temperature is maintained even during periods of strenuous exercise. When the air is half saturated, we say that the relative humidity is 50 per cent. When it contains one-fourth as much water vapor as is necessary to saturate it, the relative humidity is 25 per cent, and so on. *The ratio of the amount of water present in the air to the amount required to saturate the air at the same temperature is called the relative humidity.*

Carbon dioxide. If we blow our breath into a solution of lime-water, we notice that the latter becomes milky. This milkiness is produced by a gas, carbon dioxide, which we and all other animals exhale. The same gas is liberated into the air when coal, wood, and oil burn, and when vegetable and animal matter decay. It also issues from volcanoes. The proportion of carbon dioxide in the air is, therefore, greatest in cities and in volcanic regions, and least in the country and over the ocean. It varies from 3.5 parts in 10,000 in the country to 100 parts in 10,000 in crowded rooms.

Carbon dioxide serves as an important food for plants. Despite the huge quantities of carbon dioxide that are poured into the air continually, the amount found there does not increase, because plants are constantly absorbing the gas and returning oxygen to the air. The carbon in starch, sugar, cellulose, and other plant products is derived from the carbon dioxide of the air, which is absorbed by the leaves of plants. At one time in the history of the earth the atmosphere contained much more carbon dioxide than it does now, and vegetation in the temperate and tropical zones was more luxuriant than it is at the present time. The carbon in the coal that we use today was once in the atmosphere in the form of carbon dioxide. It was removed from the air by the trees and ferns which flourished in that early period.

Dust. The air not only contains all the gases we have mentioned, but in addition there are small solid particles called dust. These are ordinarily invisible unless they settle in layers on our furniture, but they can be seen suspended in the air when a beam of sunlight enters a darkened room. Water vapor condenses on dust particles, forming droplets that constitute clouds.

The inert gases. Helium, argon, neon, krypton, and xenon are called inert gases, because they do not react with other ele-

ments. No compound of any of these gases with another element has ever been found in nature. They are all monatomic gases; that is, they have only one atom in the molecule. Together they make up less than 1 per cent of the atmosphere. These gases are all colorless, odorless, and tasteless, and they conduct electricity better than most other gases.

Helium, in addition to its use in balloons, is finding application as a component of the gases breathed by divers and all others who find it necessary to work under water. Air under a pressure sometimes as high as 50 lb. per sq. in. is forced into their diving helmets. Nitrogen is fairly soluble in the blood, and when ordinary air is used under such great pressures, a considerable volume of nitrogen dissolves in the blood. As the diver emerges from the water, the pressure is released and the dissolved nitrogen escapes from the blood in the form of small bubbles of gas. These bubbles cause intense pain and frequently have fatal results. The disorder is often called "caisson disease," or "the bends." Helium is only slightly soluble in the blood, and at the present time a mixture of helium and oxygen, instead of ordinary air, is used in diving operations.

We have already mentioned the use of neon and argon in "neon signs." Krypton and xenon have no important uses at the present time. The presence of these inert gases in the atmosphere was not observed for more than a century after the discovery of nitrogen. The element helium was discovered in the sun by means of the spectroscope more than 25 years before it was found on the earth. By means of the same instrument, helium was found to exist in certain minerals, and later, in 1894, it was obtained from the atmosphere and from natural gases. Argon was discovered shortly afterwards. The peculiar properties of these gases led scientists to suspect that there might be other gases like them, and the careful distillation of liquid air led to the discovery of three more of them. These were named neon (the new element), krypton (the hidden element), and xenon (the stranger).

Liquid air. Since we know something about the behavior of molecules in a gas, a liquid, and a solid, it should be easy for us to understand how a gas may be changed to a liquid or to a solid. Let us see how ordinary air is liquefied. Liquid air bears the same relation to gaseous air that liquid water does to water vapor. If we wish to liquefy gaseous water, we press the molecules together until they are as close to each other as they are in liquid water, and then cool them so they will not fly apart. Air is liquefied in a similar way. The molecules of gaseous air are pressed together with an air pump until they are under a pressure of 2,000 lb. or

more per square inch; at the same time they are cooled so that they will move more slowly and have less tendency to fly apart. When the molecules are crowded closely together and are sufficiently

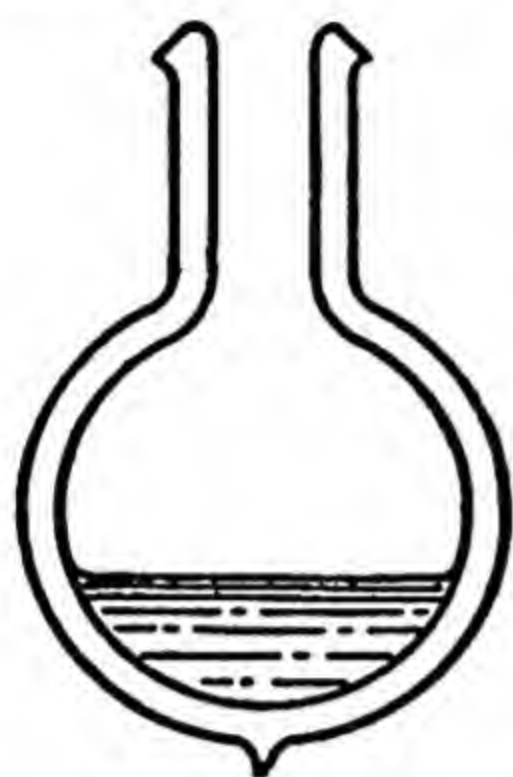


Fig. 27. A Dewar flask. The evacuated space between the two walls of the vessel retards the conduction of heat.

cooled, the air becomes a liquid which can be poured like water. On further cooling, the liquid freezes and we obtain solid air, which resembles ice. The temperature of liquid air is about 190° below zero Centigrade or 310° below zero on the Fahrenheit scale (-190°C. or -310°F.).

Containers for storing liquid air. Liquid air is stored in Dewar flasks. These flasks are familiar to everyone who has seen a thermos bottle. They consist of one flask sealed inside another with the space between the two evacuated to prevent heat from passing through the walls of the container. A thermos bottle filled with liquid air should never be stoppered, since the air changes quite rapidly from the liquid to the gaseous state and would produce an explosive pressure if not allowed to escape freely.

Questions and Exercises

1. Name the principal components of the atmosphere.
2. Define relative humidity.
3. Outline two methods of removing water vapor from air.
4. Starch, cellulose, sugar, and other vegetable products contain carbon. How do plants acquire the carbon?
5. Name the rare gases of the atmosphere.
6. State two uses for helium.
7. For what purposes are neon and argon used commercially?
8. How is air liquefied?
9. How are oxygen, argon, and neon obtained from liquid air?
10. Write the symbols for the rare gases.
11. Outline two methods for obtaining nitrogen from the air.
12. What volume of oxygen can be obtained from 300 liters of air?
13. Give evidence that air is a mixture and not a compound.
14. Which components of the air are of greatest value to plants, and which are of greatest value to animals?
15. Can you suggest a method which might be used for determining how high the earth's atmosphere extends?
16. How would you prove that air has weight?
17. Mention some good and some bad effects of dust in the air.
18. Name the three states of matter and give an example of each.

PART 2

Oxygen

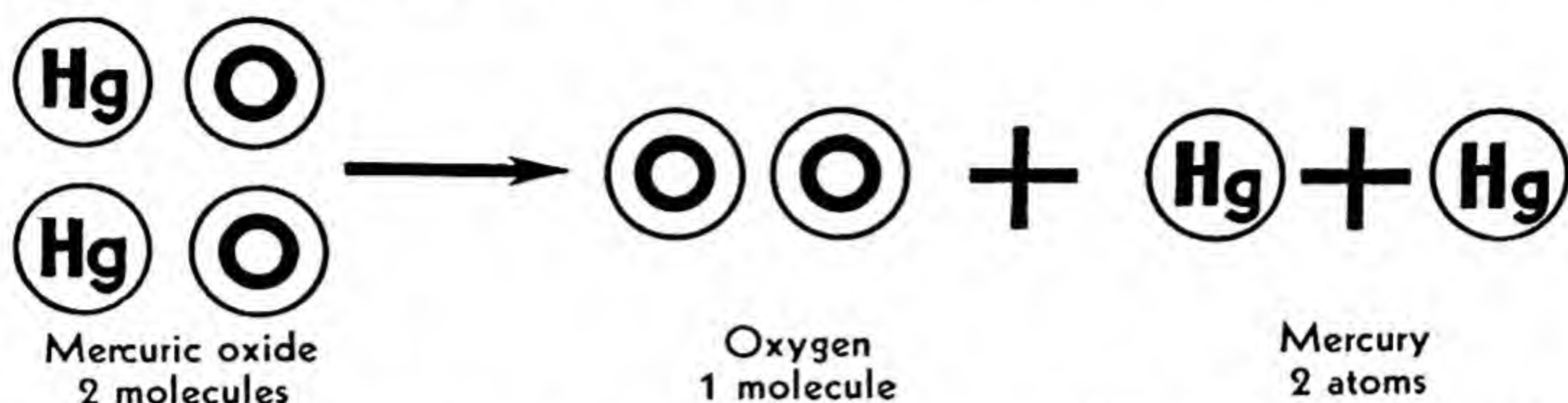
Let us study in greater detail this active substance called oxygen which is found in the air and upon which we are dependent for life.

Discovery. The discovery of oxygen in 1774 is attributed to Joseph Priestley, an English clergyman who liked to perform experiments in chemistry in his leisure time. He was especially interested in the gases which were given off when certain substances were heated. Among other things he heated the red powder, mercuric oxide, by focusing the rays of the sun upon it with a reading glass. Quite without purpose, as he admits, he thrust a lighted candle into a large amount of gas which had been given off and he was delighted with the brilliance of the flame. He had no idea, however, until a year later that the gas was connected in any way with the air which he breathed. It remained for Lavoisier to prove that this gas made up actually one-fifth of the air. Scheele, a Swedish druggist, had combined oxygen with several other elements two or three years previous to Priestley's experiments, but as his results were made known to the world at a later date than Priestley's, the latter is usually given credit for the discovery.

Occurrence. Oxygen is the most abundant element on the earth. It is found free in the air, and compounds containing oxygen constitute the majority of the substances encountered in daily life. Water is nearly 89 per cent oxygen. Limestone, granite, and other rocks and nearly all of the solid materials of the earth are compounds of oxygen with other elements. Every living plant and animal consists, primarily, of compounds containing oxygen. The human body is over 60 per cent oxygen.

Preparation of oxygen. 1. *From mercuric oxide.* One way of obtaining oxygen has already been described; namely, heating mercuric oxide as was done by Priestley and Lavoisier. Each molecule of this substance contains one atom of mercury combined with one atom of oxygen. When heated strongly, the atoms become separated from each other, oxygen gas passes off, and

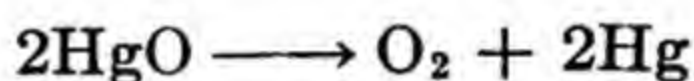
mercury remains behind. We may represent this change by a sort of chemical equation as follows:



This equation means that when mercuric oxide is decomposed, it gives or yields metallic mercury and oxygen gas.

Two molecules of mercury oxide must decompose for each molecule of oxygen gas that is formed, since a molecule of oxygen consists of two atoms of oxygen. There is only one atom in a mercury molecule.

The chemist usually writes this reaction as the chemical equation:



Methods for writing these so-called balanced equations are discussed on pages 136–137.

2. *From potassium chlorate.* Oxygen is usually made in the laboratory by heating potassium chlorate. Potassium chlorate is a

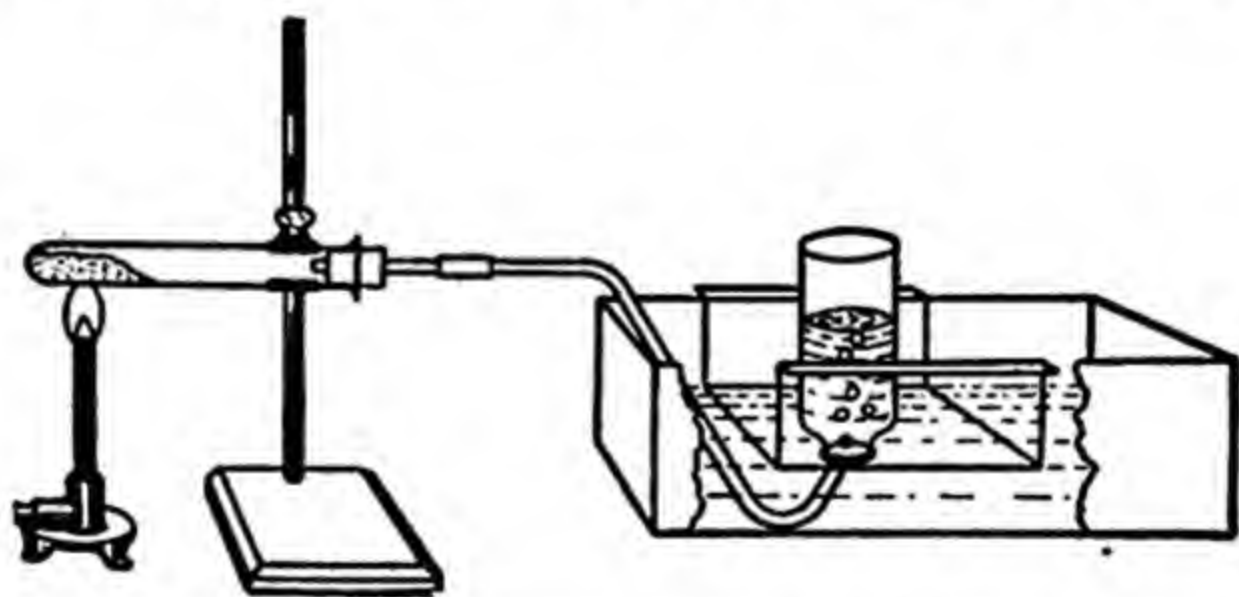


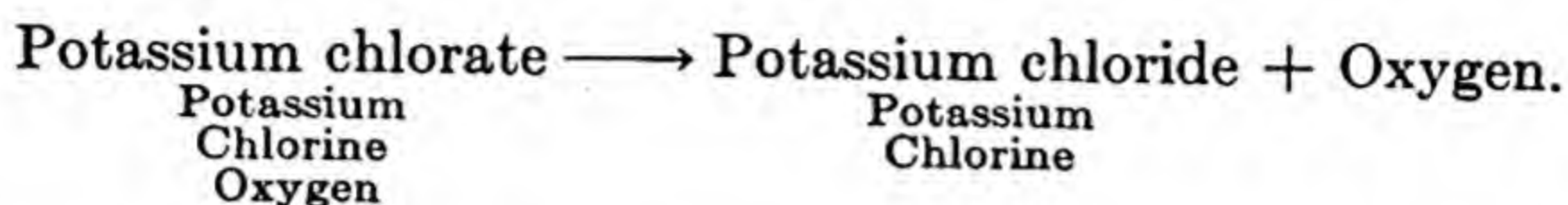
Fig. 28. An oxygen generator for use with potassium chlorate.

white, crystalline salt,* each molecule of which contains potassium, chlorine, and oxygen atoms. When heated, the oxygen atoms break away from the remainder of the molecule, leaving the potassium and chlorine atoms holding each other, in the form of potassium chloride molecules.

The experiment is carried out as follows: Potassium chlorate is placed in a glass tube (Fig. 28). A delivery tube leads from this glass tube to the receiver, which is filled with water and inverted

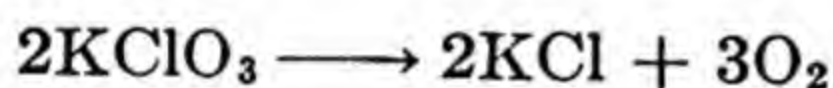
* The term *salt*, to be defined later, applies to any one of a large group of compounds.

in a tank of water. When the compound is heated, oxygen escapes through the delivery tube and displaces the water in the inverted bottle. When no more oxygen can be driven out of the potassium chlorate, a solid residue consisting of potassium chloride remains in the tube. The course of the reaction is indicated as follows:



Each molecule of potassium chlorate consists of one atom of potassium, one atom of chlorine, and three atoms of oxygen. During the heating process, the oxygen atoms pass off in pairs as molecules of oxygen gas, leaving the potassium and chlorine atoms combined in the form of potassium chloride.

The chemist expresses this behavior by the formula equation:



The temperature required to obtain oxygen when potassium chlorate is heated alone is nearly 400°C ., but if potassium chlorate and a mineral known as manganese dioxide are mixed and heated, oxygen is evolved rapidly at a temperature as low as 200°C . Examination of the contents of the tube at the end of the experiment shows that although the potassium chlorate has been changed by heating, the manganese dioxide has not. Moreover, there is exactly the same amount of manganese dioxide at the end of the reaction as there was at the beginning. In some way, which is not understood, the manganese dioxide causes potassium chlorate molecules to part with their oxygen with greater ease, without itself seeming to have entered into the reaction. Such a substance is called a *catalyst*, or a catalytic agent, or a catalyzer. There are many substances which, like manganese dioxide, accelerate chemical reactions without themselves being permanently altered in the process. A catalyst can usually be recovered unchanged after the reaction which it aids has been completed.

3. *From sodium peroxide.* Sodium peroxide is a convenient source of oxygen. Water is allowed to fall, drop by drop, on sodium peroxide, as shown by the apparatus pictured in Fig. 29.

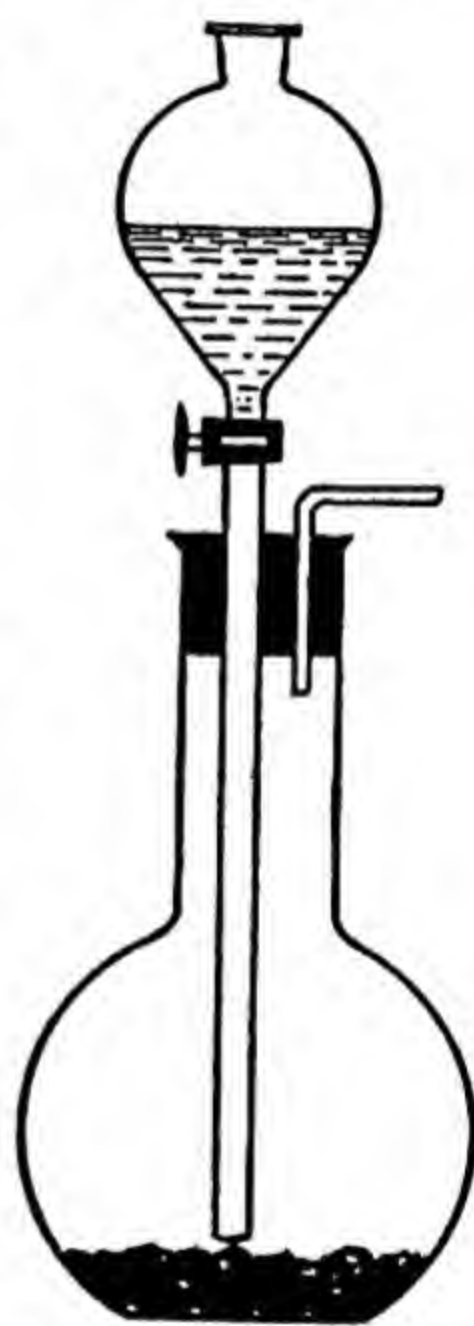
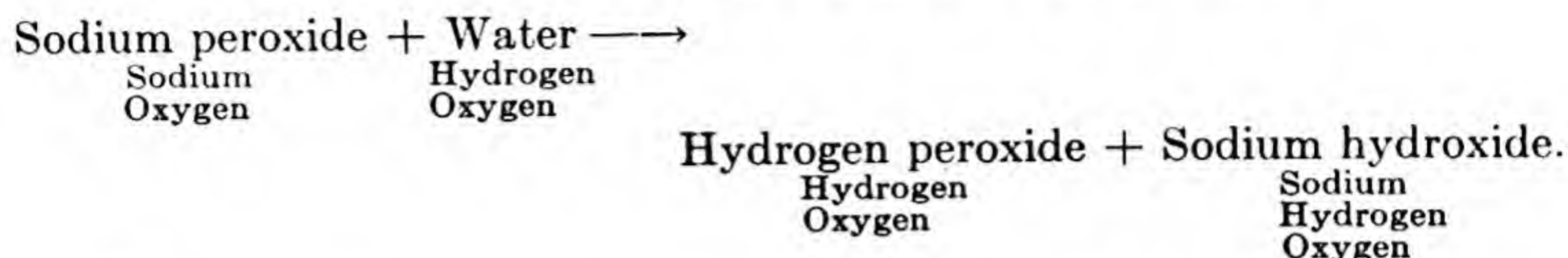


Fig. 29. An oxygen generator for use with sodium peroxide.

The sodium peroxide reacts with the water, first forming hydrogen peroxide, and the liberated hydrogen peroxide then decomposes into water and oxygen.

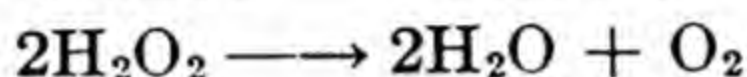
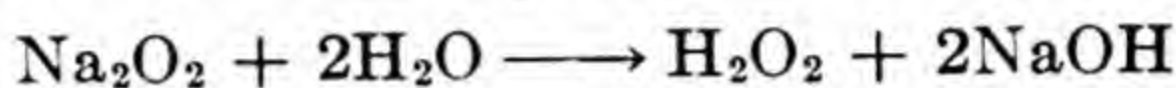
The word equations for these reactions are as follows:



Then



The chemist writes these equations:



4. *From the atmosphere.* Oxygen may be obtained from liquid air. Liquid air is permitted to evaporate until about nine-tenths of it has escaped. The remaining one-tenth is nearly pure oxygen. Nitrogen has a lower boiling point than has oxygen and it evaporates from the liquid mixture more quickly than does oxygen. Nitrogen boils at $-195.8^\circ\text{C}.$, while the boiling point of oxygen is $-183.0^\circ\text{C}.$ Hence as the liquid air is warmed, the nitrogen reaches its boiling point first, and evaporates from the solution faster than the oxygen does. As a result, some liquid oxygen remains after practically all the nitrogen has escaped. The oxygen is kept in iron cylinders under a pressure of about 2000 lb. per square inch. It is shipped to consumers in these strong containers. When a specially constructed valve in the head of the cylinder is opened, the gas emerges.

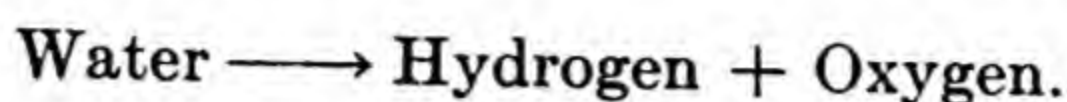


Fig. 30. Apparatus for the electrolysis of water.

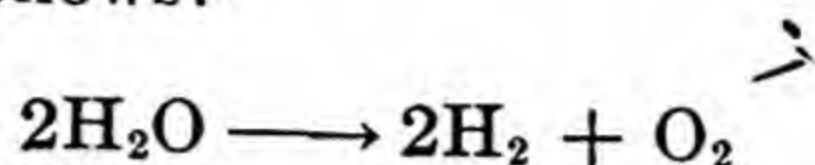
5. *From water.* Oxygen and hydrogen gases may both be obtained by passing an electric current through water containing a little sulfuric acid or sodium hydroxide. The current enters and leaves the apparatus through metallic electrodes, usually platinum, which are sealed into the glass near the bottom of each arm of the apparatus.

Each water molecule is composed of one oxygen atom and two hydrogen atoms. The electric current separates these elements. At one electrode, hydrogen atoms go off in pairs as molecules of

hydrogen gas. At the other electrode, oxygen atoms unite in pairs and escape as molecules of oxygen gas. The chemical change involved in the electrolysis may be represented as follows:



We may substitute formulas for words and represent the decomposition of water as follows:



Two molecules of water yield two molecules of hydrogen and one molecule of oxygen.

The process of decomposing a compound by an electric current is called *electrolysis*. The principle underlying this method will be explained later.

Physical properties of oxygen. Oxygen is a gas at ordinary temperatures, but changes to a liquid when cooled to -183°C . Liquid oxygen is pale blue in color, and is slightly heavier than water. Gaseous oxygen is colorless and without odor or taste. At 0°C . and under atmospheric pressure at sea level, 1 liter of air weighs 1.293 g. (grams). Under the same conditions 1 liter of oxygen weighs 1.429 g. In other words, oxygen has a greater density than has air. One hundred volumes of water dissolve about three volumes of oxygen.

The presence of dissolved gases in water may be verified by warming the water in a beaker or a pan. Bubbles of gas collect on the sides of the vessel and then rise through the water and escape at the surface before the temperature is high enough to produce steam bubbles. Ordinary faucet water behaves in this fashion as dissolved air passes off. Gases are less soluble in warm water than in cold water. The solubility of any gas in a liquid decreases as the temperature of the solvent is increased.

Chemical properties of oxygen. Both Priestley and Lavoisier found that a lighted candle burns with increased brilliance in oxygen. A wooden splinter, if lighted and then "blown out" so that it merely glows, bursts into flame and burns rapidly when thrust into a bottle of oxygen. This ability to make things burn (to support combustion) is the most conspicuous property of oxygen. Hundreds of substances will burn in oxygen. A piece of magnesium ribbon burns in oxygen with a blinding white light. Sulfur, coal, oil, sodium, and phosphorus all burn more readily in this gas than in air. We have learned that iron rusts in moist air. If a piece of steel picture wire is heated until red hot and then plunged into a bottle of oxygen, it burns rapidly, forming

the same compound of iron and oxygen which is produced when iron rusts, and glowing sparks of the compound fly in all directions.

The nature of burning. When substances burn in air or oxygen, the products formed are compounds of oxygen. Such compounds are called *oxides*. Wood contains carbon, hydrogen, and oxygen, and when wood burns two oxides, carbon dioxide and hydrogen oxide (or water), go off into the air. Hydrogen gas burns in air to form hydrogen oxide (water). Magnesium burns to a white powder called magnesium oxide. Sulfur forms sulfur oxide (usually called sulfur dioxide); sodium burns to sodium oxide; phosphorus, to phosphorus pentoxide. Iron rust is iron oxide. These reactions may be expressed in "word equations" as follows:

Wood + Oxygen	→	Carbon (di)oxide + Hydrogen oxide (water).
Hydrogen + Oxygen	→	Hydrogen oxide (water).
Magnesium + Oxygen	→	Magnesium oxide.
Sulfur + Oxygen	→	Sulfur (di)oxide.
Carbon + Oxygen	→	Carbon (di)oxide.
Sodium + Oxygen	→	Sodium oxide.
Phosphorus + Oxygen	→	Phosphorus (pent)oxide.
Iron + Oxygen	→	Iron oxide.

Formula equations for these reactions may be found on pages 139 and 140. Under favorable conditions, nearly all metals combine with oxygen to form oxides.

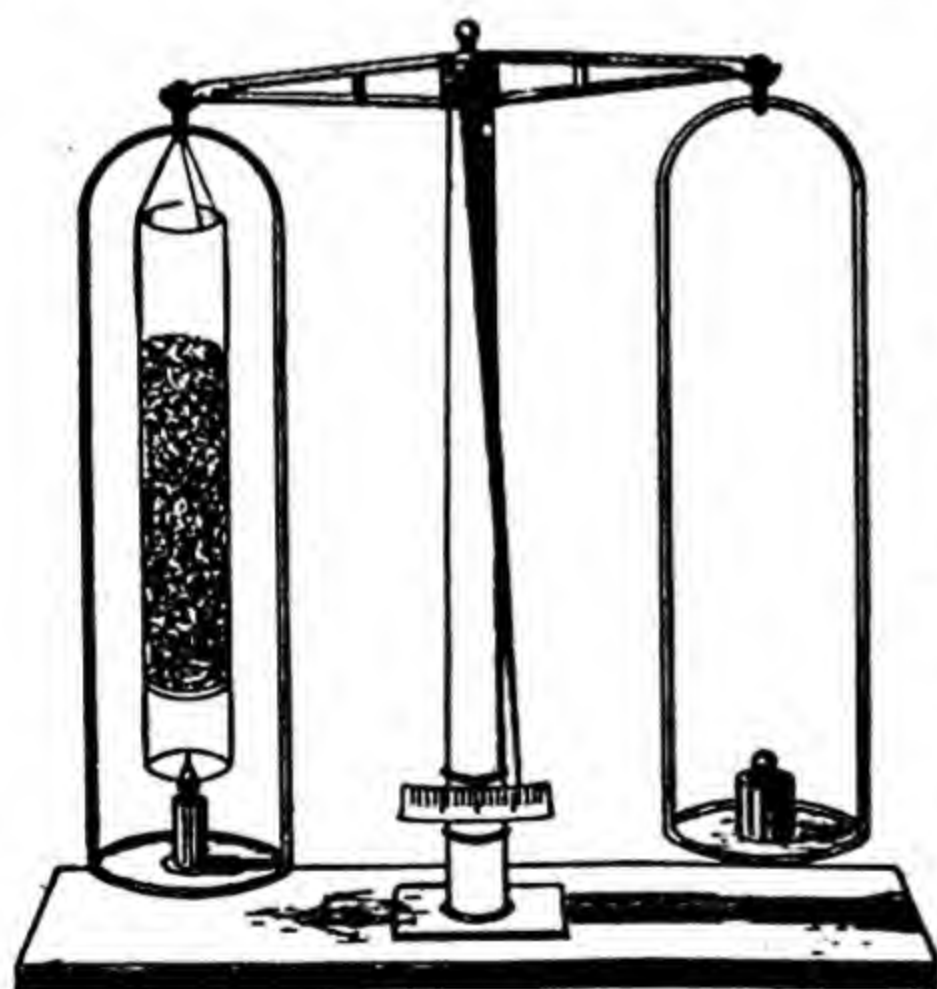


Fig. 31. The weight of the carbon dioxide and water formed is greater than the original weight of the candle.

When a substance burns in oxygen or air, the compounds formed contain the original weight of the substance plus the weight of oxygen with which it combines during the burning process. An experiment illustrating this principle is shown in Fig. 31. A candle is placed under a vessel filled with soda lime on one pan of a balance, and weights are placed upon the opposite pan until the two sides are balanced. The candle is then lighted, and it gradually grows shorter, obviously diminishing in size and weight; but at the same time the pan on which the candle rests gradu-

ally goes down, indicating that the load on this side of the balance is becoming heavier. The products formed when a candle burns are carbon dioxide and hydrogen oxide. At the temperature of the flame these products are gases. Both are absorbed by soda lime.

The experiment shows that the carbon dioxide and water thus formed weigh more than the original candle.

Oxidation. Union of oxygen with another element to form an oxide is one type of the process known as *oxidation*. (A more general definition of this term will be given later.) Oxidation may take place rapidly, as in the explosion of a mixture of gasoline and oxygen; or it may occur at a moderate rate, as in the burning of a candle; or it may proceed slowly, as in the rusting of iron. The term *combustion*, or burning, is usually applied when the oxidation takes place rapidly enough to be accompanied by light and noticeable heat. We have all seen a house burn, and know that both light and heat are given out. This is a typical example of combustion, or rapid oxidation.

Heat is given out also during slow oxidation. If we were to measure the heat given out when a piece of magnesium burns rapidly in oxygen, we should find that it is equal to the heat given out by the same weight of magnesium when it is allowed to oxidize slowly. However, during the latter process the heat is given out gradually over a considerable period of time, so that it is not noticeable.

Spontaneous combustion. The heat given out by slow oxidation plays an important part in what we call spontaneous combustion. Turpentine and linseed oil oxidize when in contact with air. If rags soaked with paint containing these substances are placed in a closet or box where the air does not circulate freely, the heat given out during slow oxidation is not carried away and the cloth gets warmer and warmer. Finally the oil or turpentine reaches the kindling temperature and bursts into flame. That is, at the kindling temperature the oxidation becomes rapid and is accompanied by light and noticeable heat. The *kindling temperature* of a substance is the lowest temperature at which the substance will continue to burn with the emission of light.

Many industrial buildings have been destroyed by spontaneous combustion. The fine flour dust which circulates through the air in a flour mill is oxidized by the oxygen of the air; the oxidation gives out heat which may raise the temperature of the particles to the kindling point. If this temperature is reached, the flour particles catch fire, and the result is an explosion similar to that which takes place when a spark is produced in a gas-filled room

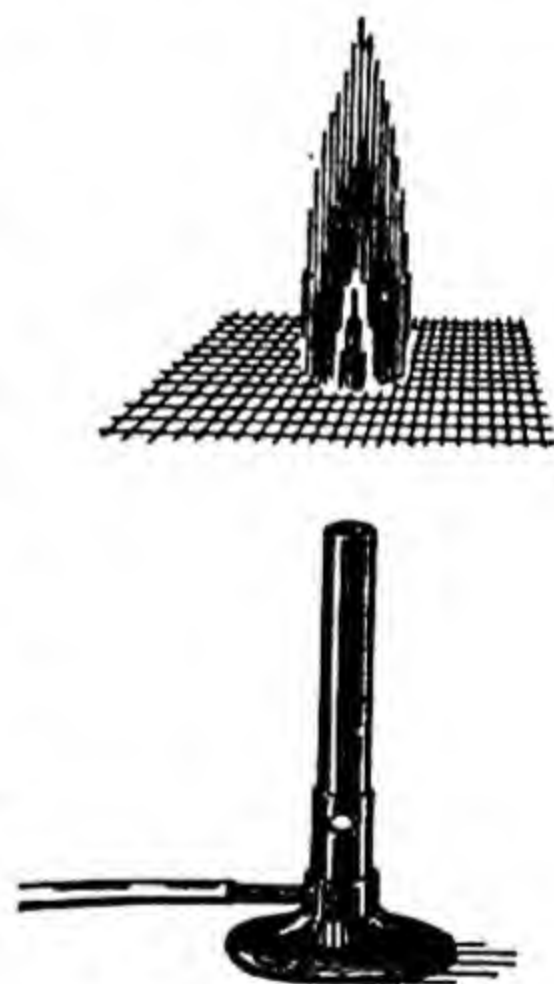


Fig. 32. The wire gauze conveys away the heat so rapidly that the gas below the gauze does not reach its kindling temperature.

or when the light of a match is used to determine the amount of gasoline in the tank of an automobile.

If a substance which is burning becomes cooled below its kindling temperature, rapid oxidation stops. Water poured on a burning house puts out the fire because it lowers the temperature of the wood below its kindling point. When we wish to build a campfire, we usually fan the fire until it becomes well established;

but if a small blaze is fanned too rapidly, the fire goes out. Can you explain why? Similarly, if a burning gas is cooled below its kindling point, the fire goes out. A gas cannot burn at a temperature below its kindling point.

If iron wire gauze is held over a gas jet, the gas may be ignited above or below the gauze, without igniting the gas on the opposite side of the gauze. Iron is a good conductor of heat. The wire conducts heat away from the flame very rapidly. The gas which is separated from the flame by the gauze is not heated to its ignition temperature and, therefore, does not take fire.

Sir Humphry Davy used this principle in his invention of the miner's safety lamp. Combustible gases often issue from crevices in coal mines. Such gases form explosive mixtures with air in the mines. Miners' lamps, igniting explosive mixtures of this kind, have caused

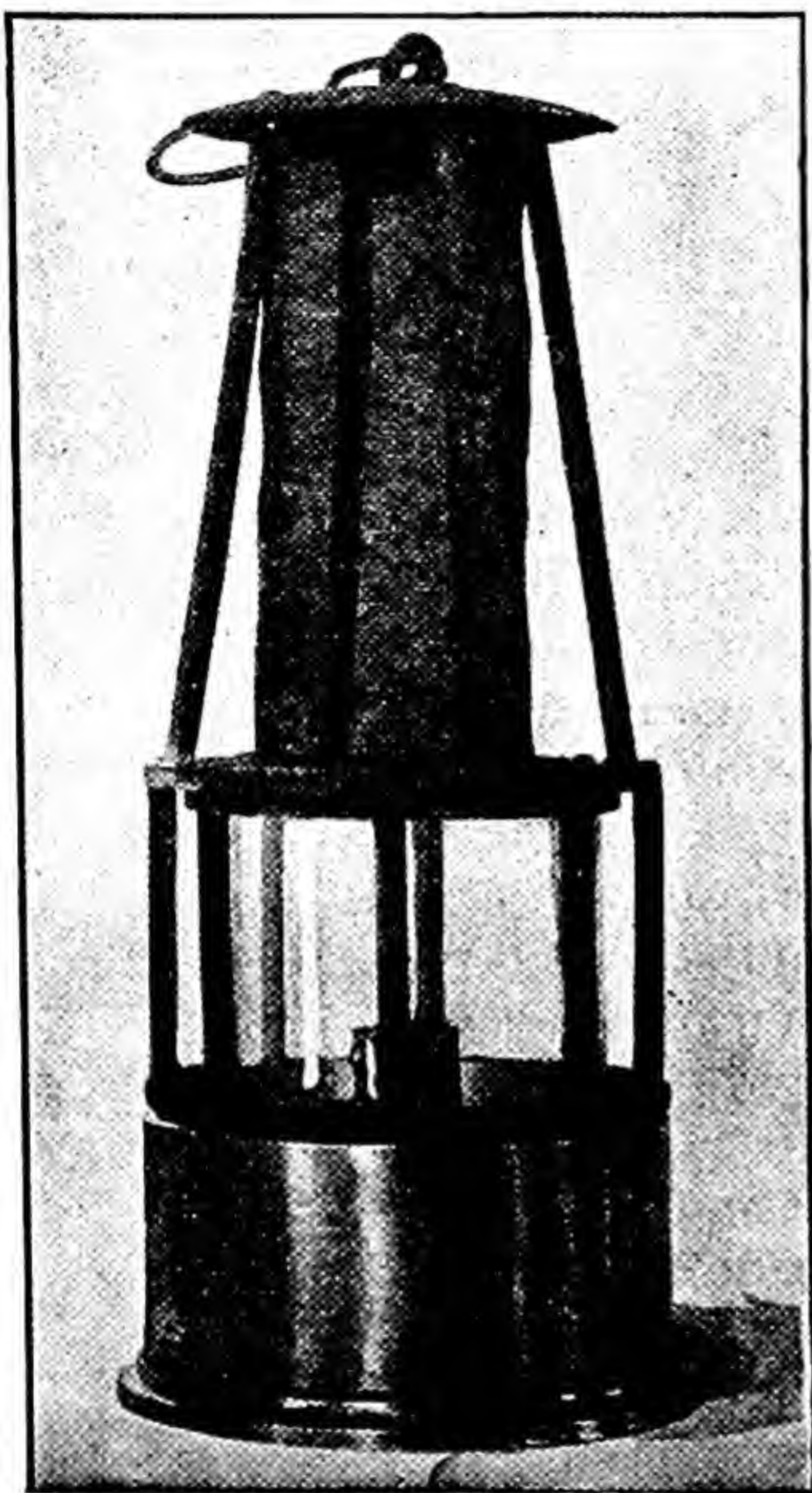


Fig. 33. The Davy safety lamp.

many disasters. Davy constructed a lamp in which the flame is completely surrounded by a fine wire gauze. When the combustible gas accumulates in a mine, the flame sets fire to it, causing a small explosion within the lamp; but the gauze conducts the heat away so rapidly that the gas mixture outside the lamp does not reach its kindling temperature. A series of small explosions in the lamp is a signal to the miner that he is in a dangerous atmosphere. He leaves the mine until the atmosphere is cleared.

The Bunsen burner. The Bunsen burner was the first successful device for using gas conveniently for heating. All gas burners.

including our kitchen stoves and gas furnaces today, are made according to the principle of the Bunsen burner. Gas under pressure enters the barrel of the burner through a small orifice. There is a hole near the base of the burner which provides for the admission of air. As the gas molecules rush past this hole, air is drawn into the gas stream. The quantity of gas entering the barrel is controlled by a stopcock in the gas pipe, and the supply of air is regulated by adjusting the size of the opening in the collar or in the base of the burner.

The amount of air (or oxygen) taken into the burner is not sufficient for the complete combustion of the gas, and the additional oxygen required for this purpose is taken from the air surrounding the flame. If all the oxygen had to be taken from the air surrounding the flame, the flame would be long and smoky. Soot or smoke is formed when the gas, whose molecules are made of carbon and hydrogen atoms, gets hot enough to decompose into these elements, but lacks the oxygen necessary to convert these decomposition products completely into carbon dioxide and water. You can easily prove this by closing the hole in the collar of the burner. A yellow, luminous flame results. If a piece of glass or porcelain is held in this flame for a short time, it becomes covered with a deposit of soot. The yellow color of the flame is caused by the carbon particles being heated to incandescence in the flame. As soon as they strike a cold surface, they are cooled and they stop glowing. They become tiny black particles of carbon which we call soot.



Fig. 34. A Bunsen burner.

When part of the needed oxygen is mixed with the gas in the tube of the burner, the flame becomes nonluminous; that is, it is free from light-radiating particles of hot carbon because these particles burn completely to carbon dioxide. The nonluminous gas flame is much hotter than the luminous one, because in the former both the hydrogen and the carbon are burning completely.

Frequently kitchen gas ranges deposit soot on cooking utensils. Soot is an indication that there is not enough air being mixed with the gas before it enters the burner. To remedy this we have the openings at the base of the burners made larger so that more air may enter and mix with the gas stream on its way to the burner. In a correct mixture both the carbon and the hydrogen in a gas burn completely.

A gas flame has an inner cone which contains unburned fuel gas, and surrounding this cone is a very hot zone where complete oxidation takes place. At the tip of the flame and at its extreme outer edge there is an excess of oxygen or air. A metal held at the tip of the flame is rapidly oxidized. Some oxides when held in the tip of the inner cone are reduced or deoxidized, oxygen being removed from the oxide by the hot gas.

We can prove by a simple experiment that the inner cone of the flame is composed of gas which is not burning. Pass a common pin through a match stick about one-half inch below the tip, so that the match is suspended at the middle point of the pin. If

the match is passed quickly through the outer edge of the Bunsen flame, the head of the match may be placed in the middle of the cone, with the arms of the pin resting on the edges of the barrel, as shown in Fig. 35. A match will remain unburned in the cone for a long period of time, definitely showing that the gas in the cone is neither burning nor hot enough to ignite the match.

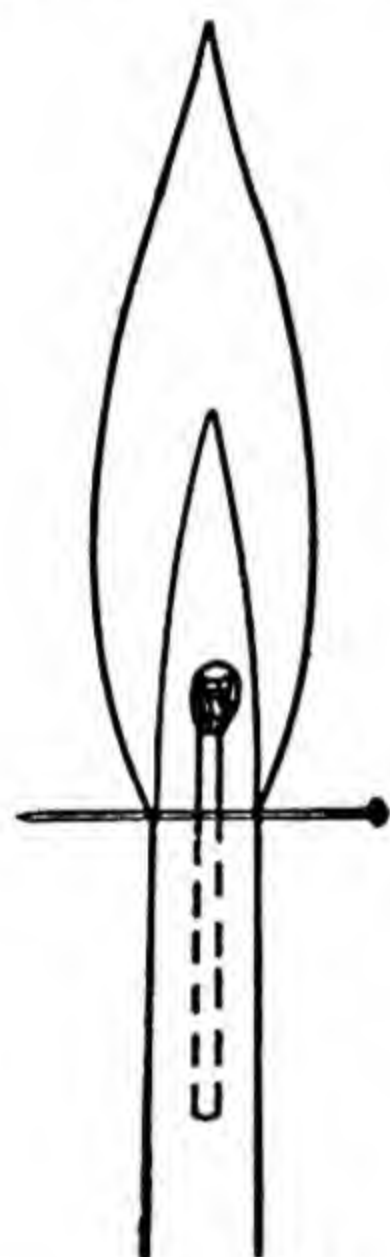


Fig. 35.
Inner cone of a
flame.

Oxygen in relation to life. Oxygen is essential to life; but if a person were to breathe pure oxygen continually, reactions in the blood stream would go on too rapidly. The oxidation processes in the body would increase as they do when a lighted candle or splinter is placed in a bottle of oxygen. However, pure oxygen is often administered, in place of air, to people who are sick. Pneumonia patients suffer from a reduction of the breathing area of the lungs; so pure oxygen is given them in order that a sufficient amount of oxygen may reach the blood stream.

Oxygen is administered also in cases of asphyxiation and drowning. Aviators and mountain climbers are equipped with cylinders of compressed oxygen when they expect to reach high altitudes. Firemen entering buildings filled with suffocating fumes, and rescue parties entering mines, also carry cylinders of oxygen.

Ozone

Anyone who has entered a room where X rays are being used is probably familiar with the odor of ozone. X rays convert some of the oxygen of the air into ozone. Electric sparks and flashes of lightning in air change small quantities of oxygen into ozone. Ordinary oxygen consists of molecules each of which contains two atoms of oxygen, while each molecule of ozone consists of three atoms of oxygen. When oxygen molecules are

changed into ozone molecules by an electric spark, the reaction shown in Fig. 36 takes place. Ozone is a colorless gas with a distinct odor. It decomposes when heated, yielding ordinary oxygen. Two molecules of ozone yield three molecules of oxygen.

The ozone molecule is unstable even at room temperatures. There is a tendency for the third oxygen atom to split off and attach itself to some other atom or molecule, leaving an oxygen molecule behind. Ozone, therefore, is a powerful oxidizing agent. It bleaches colored fabrics by decomposing the dyes and changing them to colorless substances. It kills bacteria and is used in some places to destroy the germs in city water supplies. The higher regions of the atmosphere contain ozone formed from oxygen by some of the ultraviolet rays of the sun. The ozone thus formed

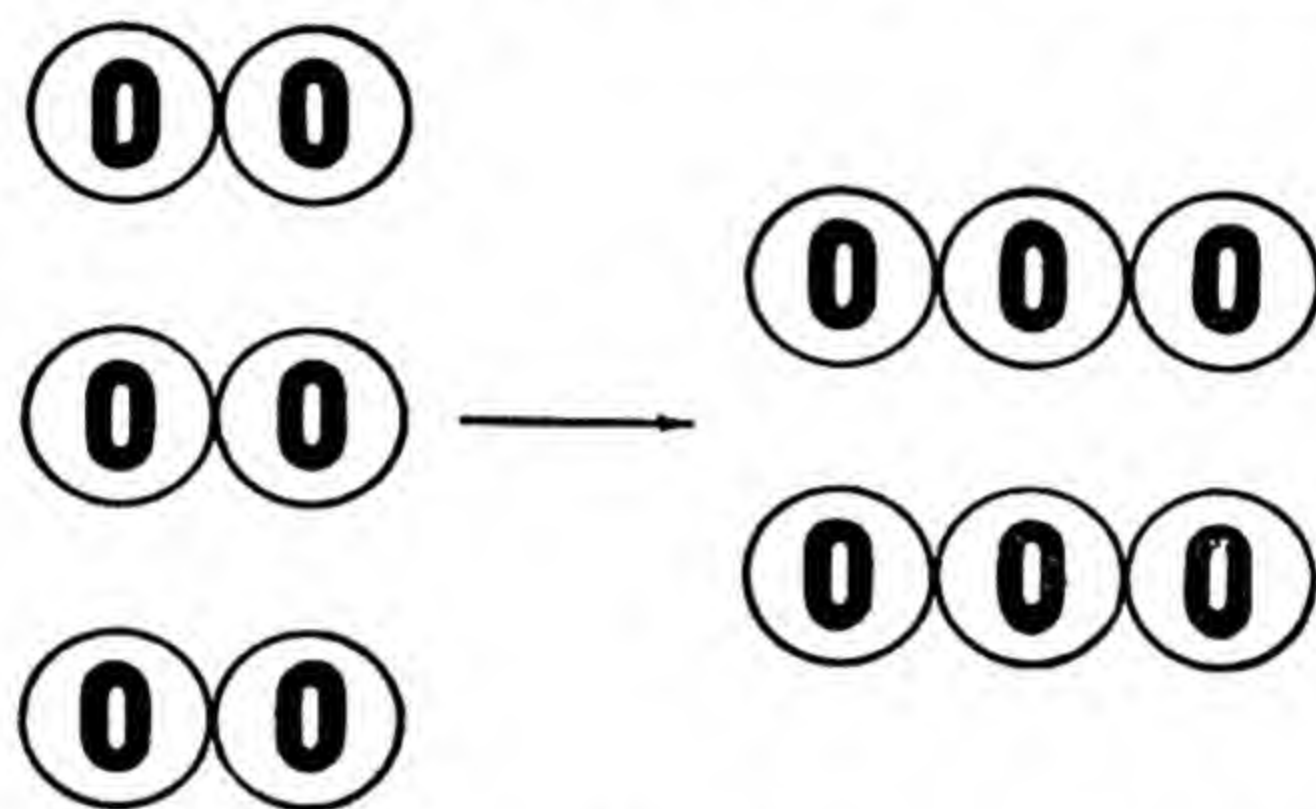


Fig. 36. Three molecules of oxygen gas, O_2 , yield two molecules of ozone gas, O_3 .

in the atmosphere absorbs most of the ultraviolet light of the sun, and this is fortunate for us, for these rays of short wave lengths would be detrimental to plant and animal life. Short exposures to ultraviolet light may be beneficial, but long-continued exposures would be disastrous.

The light that comes from the sun is made up of many kinds of rays. Some of these rays if seen alone would be red; others would be yellow, green, blue, or violet. In a rainbow all these colors appear, for droplets of water separate the various rays of light that come from the sun. The separation of these rays can be accomplished also by a glass prism. A violet color is produced by the shortest waves of light that the eye can see, and red corresponds to the longest waves the eye can see. The sun gives off shorter waves than those that produce violet light. We cannot see these short waves, but they act on a photographic plate just as ordinary light does. We call these invisible rays *ultraviolet light*. Longer waves than those that produce red light are called *infrared rays*.

Allotropic forms of elements. Oxygen and ozone are two different gases whose molecules are made entirely of oxygen atoms. When two or more substances in the same physical state (oxygen and ozone are both gases) have their molecules composed entirely of atoms of the same element but in different numbers or arrangements, we call them *allotropic forms* of that element. Thus oxygen gas and ozone are allotropic forms of oxygen. We shall learn later that other elements, such as carbon, sulfur, and phosphorus, exist in several allotropic forms.

Questions and Exercises

1. Name several substances which contain oxygen.
2. Approximately what fraction of the air is oxygen?
3. Is oxygen a gas, a liquid, or a solid?
4. How can oxygen be prepared from water? How is it obtained from air?
5. What is combustion?
6. Explain why the products of combustion obtained from coal weigh more than the coal weighed.
7. Give one definition of the term *oxidation*.
8. How is the temperature of the human body maintained?
9. What is wrong when the flame of a gas burner is smoky and luminous?
10. What is meant by the *kindling temperature* of a substance?
11. Explain the operation of the Davy safety lamp.
12. Why should oily rags not be left in a pile for a long time?
13. What is the difference between a molecule of oxygen and a molecule of ozone?
14. State some of the properties of ozone.
15. What is a catalyst? Give an example.
16. A small flame can be extinguished by covering it with a blanket. Explain.
17. Explain why a candle flame can be extinguished (a) by pinching the wick, (b) by blowing, (c) by placing the candle in a closed jar, (d) by touching the wick with a piece of copper gauze.
18. Would it be easy or difficult to start a fire if the atmosphere were composed of pure oxygen? Would it be easy or difficult to extinguish a fire under this condition?
19. A test tube is filled with water, then inverted in a vessel containing water, and warmed. A small volume of gas accumulates above the water in the tube. Is the gas air or steam? If it were steam, would it remain in the gaseous state when cooled? Does the solubility of air in water increase or decrease when the temperature of the water is increased?
20. What is an oxide?

21. Chemical laboratories are often equipped with fire blankets. Explain their use.

22. Some of the American Indians started their fires by the friction of one piece of wood upon another. Explain.

23. Explain the action of water in extinguishing a fire.

24. Describe four methods of preparing oxygen.

25. Who discovered oxygen?

26. The weight of the atmosphere resting upon each square inch of the earth's surface is approximately 15 pounds. The air is 23 per cent oxygen by weight. Assuming that the area of the earth is 197,000,000 sq. mi., calculate the weight of oxygen in the atmosphere.

27. If you were handed two test tubes, one filled with oxygen and the other with air, how would you prove which one was filled with oxygen?

28. Write "word equations" for the reactions that take place when the following elements are burned in oxygen: aluminum, carbon, sulfur, sodium, zinc, potassium, and copper.

29. Why are all iron and steel structures, like bridges and the frames of buildings, painted?

PART 3

Hydrogen

In our discussion of the methods for preparing oxygen, we learned that if water is electrolyzed, oxygen gas appears at one electrode, while at the same time hydrogen gas collects at the other electrode. We also found that the hydrogen formed has just twice the volume of the oxygen formed during the electrolysis.

The name *hydrogen* is known to all of us who are familiar with its use in dirigibles. Hydrogen is the lightest substance that has ever been discovered on our earth, or in the sun and stars. It is only one-fourteenth as heavy as air. A balloon filled with hydrogen rises readily through the air. The *Graf Zeppelin* (a famous German airship) required 3,500,000 cu. ft. of gas. It used more than 9 tons of hydrogen and had a lifting capacity of approximately 120 tons. Hydrogen has one disadvantage in this use—it burns readily. Many hydrogen-filled airships have been destroyed by fire. There is always danger in the use of inflammable gases.

Discovery of hydrogen. As early as the sixteenth century, chemists noticed that bubbles of gas rise from a metal which is covered with sulfuric acid. It was not until 1776, however, that the nature of the gas was discovered. In that year Henry Cavendish caught samples of the gas, made by placing several metals (zinc, iron, and tin) in sulfuric acid, and found in each case that the same gaseous substance was evolved. Similar results were obtained by substituting hydrochloric acid for sulfuric acid. Cavendish believed that the gas came from the metal, and not from the acid. He succeeded in making his gas combine with oxygen, which had been discovered by Priestley two years earlier. To his great astonishment, water was the product of this combination. Lavoisier named the new gas hydrogen, meaning “producer of water.”

Occurrence of hydrogen. Hydrogen in the free state does not occur to any great extent on the earth. The atmosphere contains mere traces of hydrogen gas. It issues with other gases from volcanoes. The gases surrounding the sun and some stars contain

large quantities of hydrogen. In combination with other elements, hydrogen occurs in many familiar substances, such as water, acids, and all living plant and animal cells. Natural gas, petroleum, and paraffin are composed of hydrogen and carbon.

Preparation of hydrogen. If we wish to prepare hydrogen in the laboratory, we must start with something which contains hydrogen. We should also choose a compound which will give up hydrogen readily.

Preparation from water. Since water is inexpensive and gives up its hydrogen readily in certain circumstances, it is an important source of this gas. There are four common methods for preparing hydrogen from water:

- (1) The electrolysis of water.
- (2) The action of metals on water.
- (3) The action of steam on hot carbon.
- (4) The action of steam on methane gas.

The electrolysis of water. Water is decomposed by electricity in making hydrogen for use in the industries wherever electrical power is abundant, as at Niagara Falls. The laboratory method has already been described in connection with the preparation of oxygen.

Action of metals on water. This method is often used in the laboratory as a source of hydrogen. When a small piece of the metal sodium is placed on the surface of water, it reacts energetically with the water. In fact, sodium reacts so readily even with the water vapor in the air that it must be kept immersed in gasoline or kerosene. Since sodium is lighter than water, it floats, and the floating metal reacting with the water gives out enough heat to change the sodium to a globule of melted metal. During the reaction, hydrogen gas is liberated and the sodium



Fig. 37. Henry Cavendish (1731-1810) was a wealthy and eccentric recluse. He was interested in experimental work and cared nothing for fame. His experiments were performed with great care, and his discoveries were important, but he did not publish his findings. Most of the results of his labors were published by others, who later had access to his notebooks. He avoided society and even had a back stairway built to his apartment so he could enter and leave his rooms without meeting anyone. The portrait shown here is a copy of the only picture of Cavendish in existence. It was painted surreptitiously, in installments, by an artist who knew he could never get the picture in any other way.

hydroxide, or lye, formed at the same time, remains behind. Care must be taken during the experiment to avoid being burned with the flying particles of sodium. Sometimes the action becomes

so rapid, especially if too large a piece of sodium is used, that explosion occurs, showering small bits of molten sodium into the air. Danger is avoided by holding a large glass plate between the experimenter and the reaction vessel.

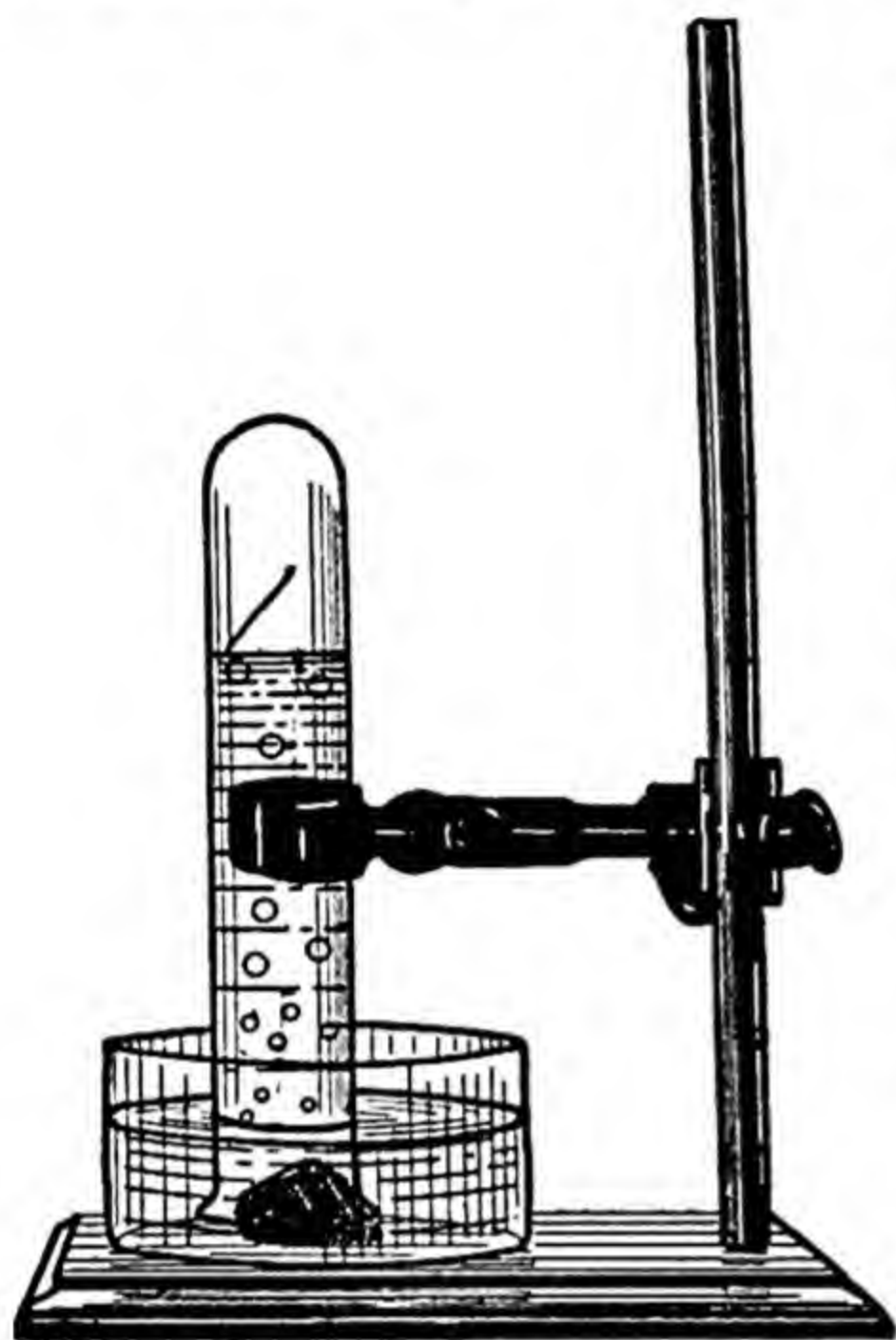
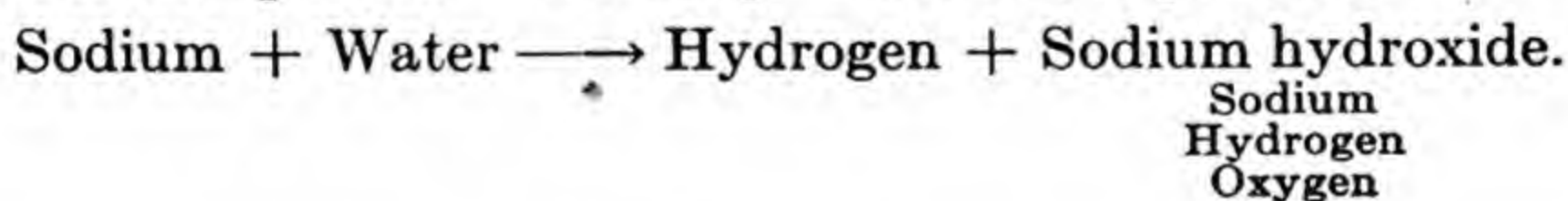


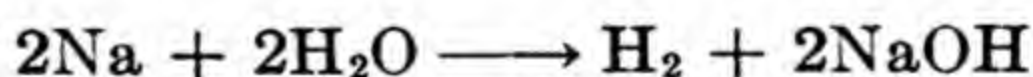
Fig. 38. Sodium decomposes water, yielding sodium hydroxide and hydrogen.

If we wish to collect the hydrogen in a test tube, the sodium is wrapped in a piece of copper gauze and placed under the test tube, which is filled with water and inverted in a larger vessel which also contains water. The hydrogen liberated during the reaction, being very light, bubbles up through the water to the top of the test tube, driving the water downward and out of the tube. If a large enough piece of the metal has been used, we shall have the tube filled with hydrogen in a very short time.

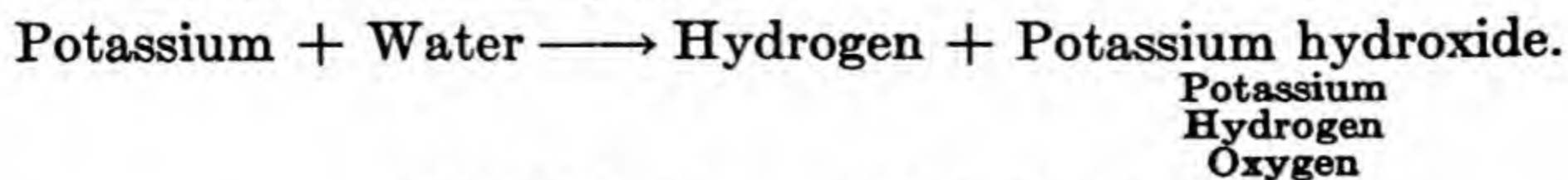
When sodium reacts with water, it liberates only one of the hydrogen atoms contained in each molecule decomposed. We may write the equation:



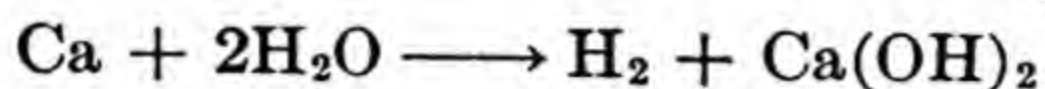
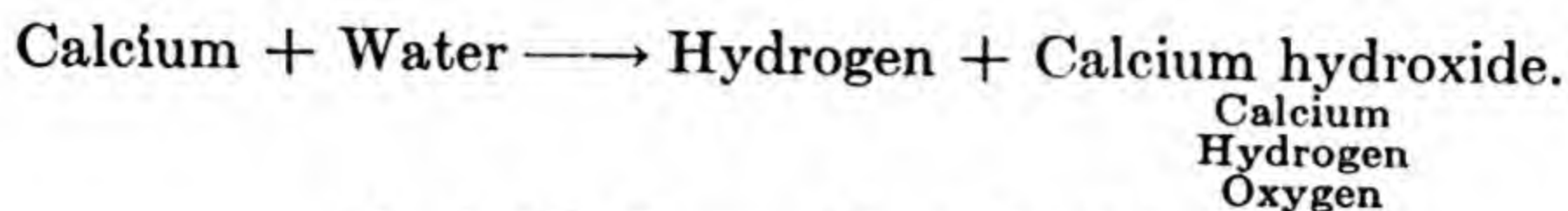
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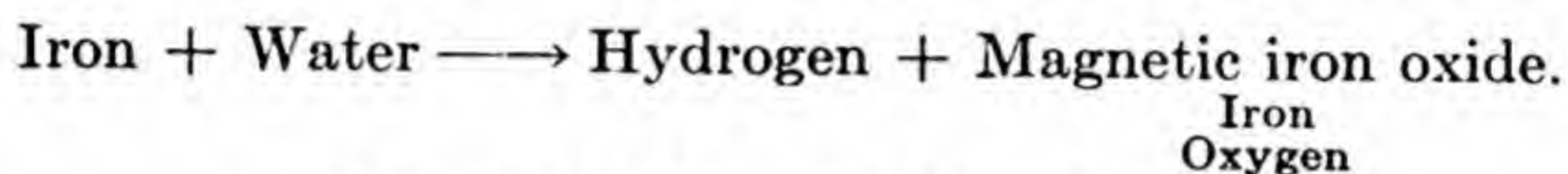
Potassium is a metal which looks like sodium; it is white, soft enough to be cut readily, and must be kept under gasoline or kerosene. It reacts with water even more violently than sodium does. It gives out so much heat that the hydrogen formed is heated to its kindling point and burns on the surface of the water as fast as it is formed. When the reaction is complete and the piece of potassium has disappeared, potassium hydroxide is found dissolved in the remaining water.



Calcium is a fairly light metal, but harder than sodium and potassium. It reacts with water, liberating hydrogen and leaving calcium hydroxide in solution. A solution of calcium hydroxide is ordinary limewater.



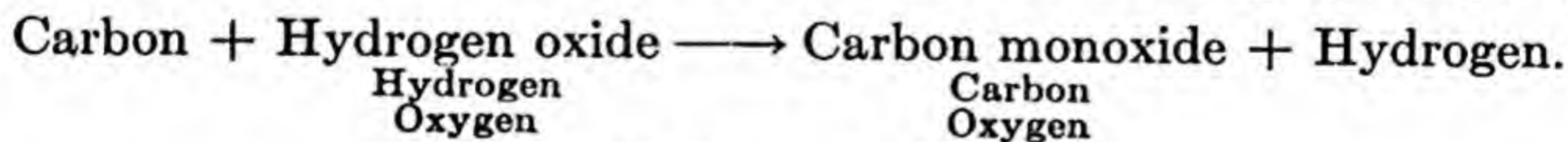
Less reactive metals like magnesium, zinc, and iron react slowly with water. When such metals are used to release hydrogen from water, it is necessary to have the metal in the form of fine filings and very hot, and the water in the form of steam. When steam is passed over hot iron, hydrogen is liberated and a compound known as magnetic iron oxide is formed. In this case both atoms of hydrogen in the water molecule are driven out by the iron:



This method is often used in making hydrogen for filling balloons, since iron is comparatively inexpensive.

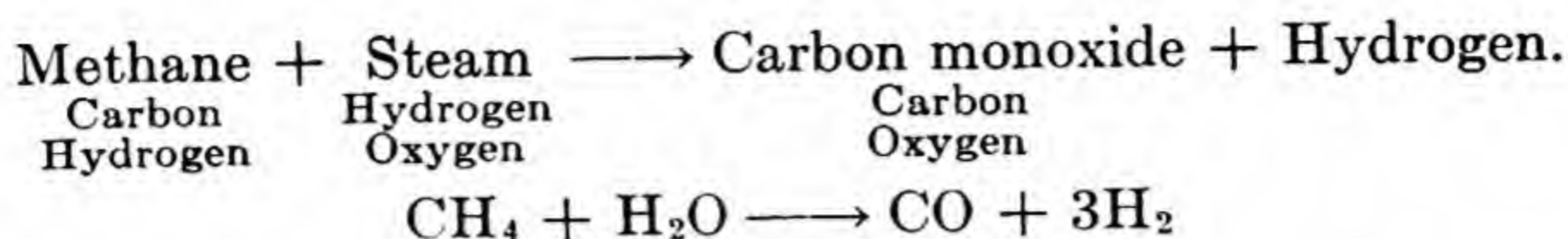
It is extremely fortunate for us that iron and aluminum do not react readily with water. If they did, we should not be able to boil water in any ordinary tea kettle. We should be forced to use cooking utensils made of glass or pottery, copper, gold, silver, or platinum. The so-called "noble" metals do not replace the hydrogen in water.

Water-gas method. If steam is passed over hot carbon (coke is generally used) a mixture of gases known as "water gas" is produced. The hot carbon removes the oxygen from the water molecule, forming carbon monoxide, and liberating hydrogen gas.



The carbon monoxide and hydrogen may be separated by subjecting the mixture to a pressure twenty times as great as that of the atmosphere and at the same time cooling it to -200°C . Hydrogen remains in the gaseous state under these conditions, and carbon monoxide becomes a liquid.

Methane-steam method. In recent years much hydrogen has been made by heating the hydrocarbon, methane, with steam.



The hydrogen may be separated from the carbon monoxide as indicated above.

Preparation from acids. Many metals which liberate hydrogen from water only at high temperatures react with acids at ordinary temperatures. All acids contain hydrogen, which is easily liberated by the metals which we used in the preparation of hydrogen from water. Metals like sodium, potassium, and calcium, however, react so violently with acids that they are never used for this purpose in the laboratory. The metals ordinarily used are zinc and iron, although aluminum and magnesium also react readily with acids. The acids usually employed are hydrochloric acid and sulfuric acid.

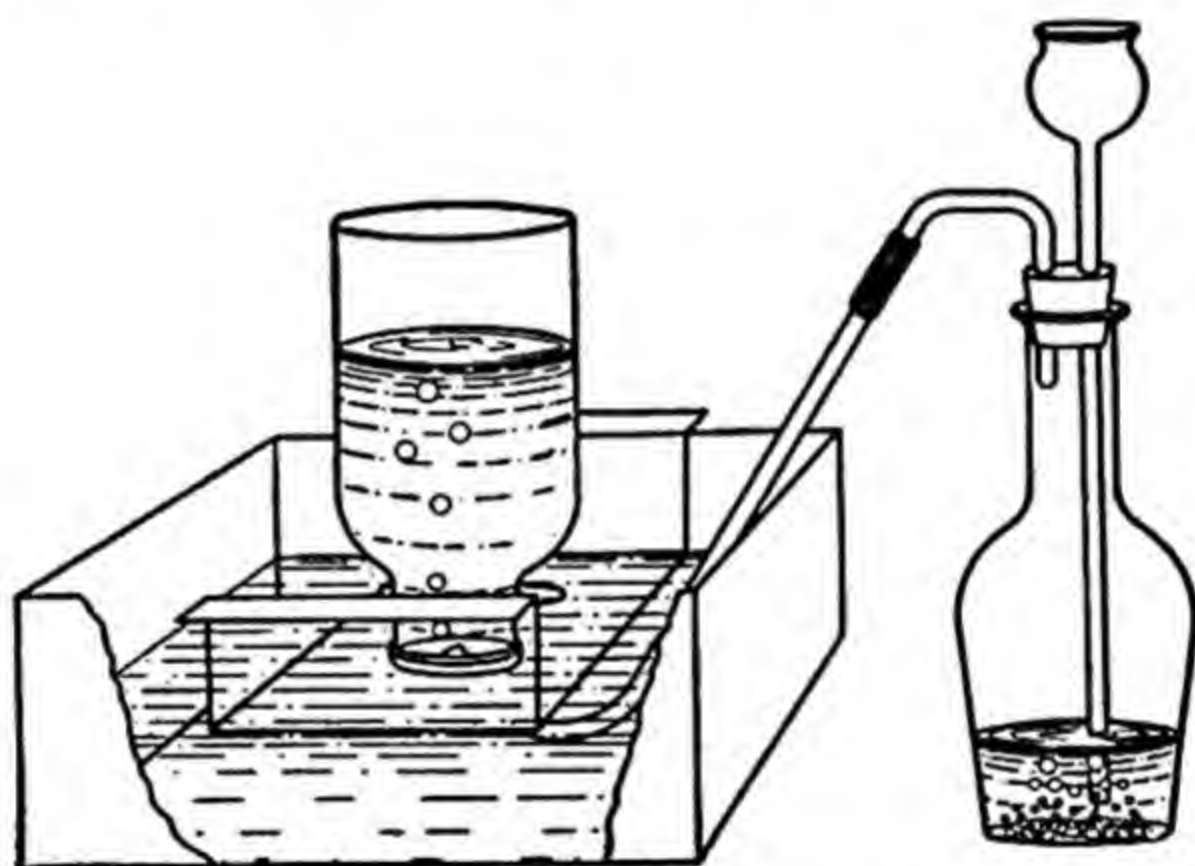
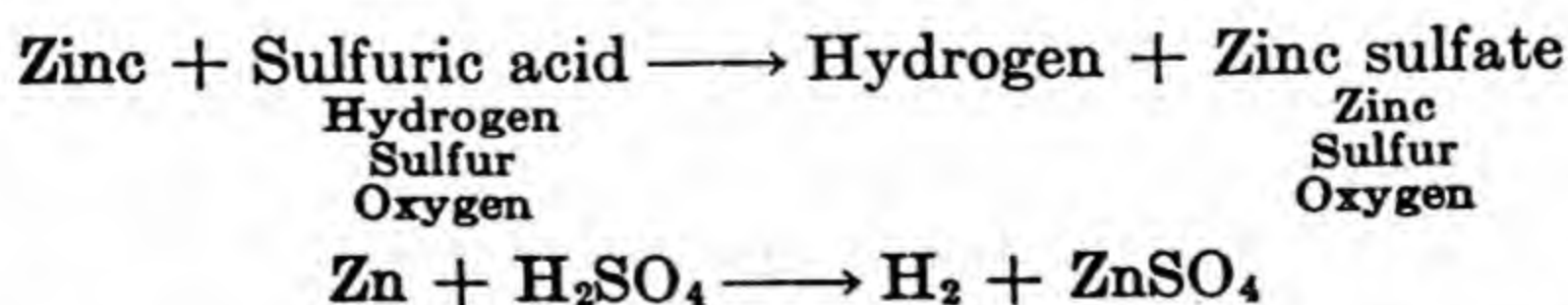
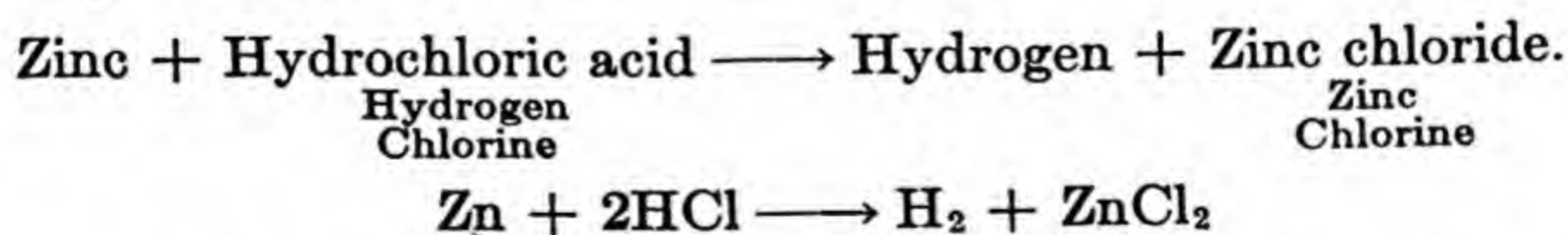


Fig. 39. Zinc acts upon hydrochloric acid, releasing hydrogen gas.

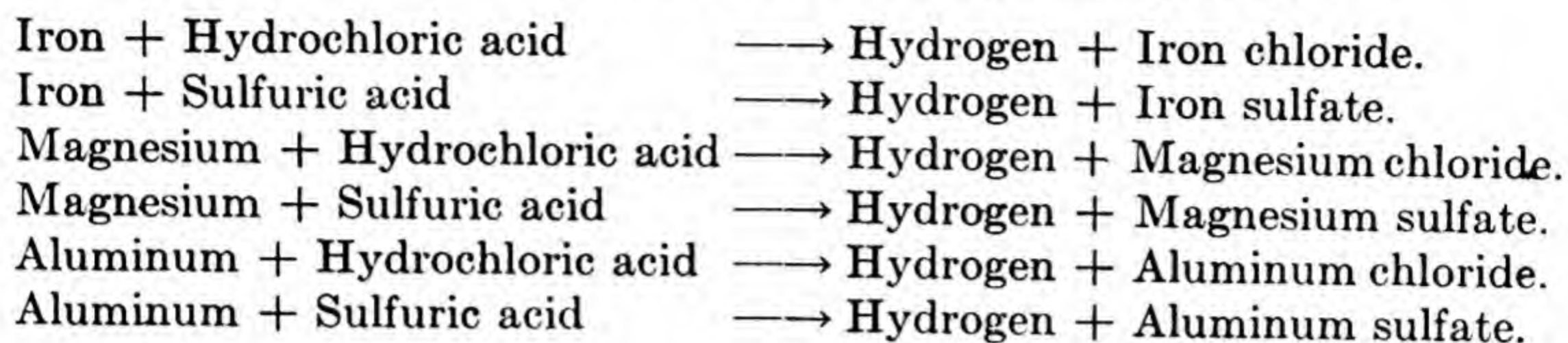
When zinc is used with hydrochloric acid or sulfuric acid, the following reactions occur:



The zinc displaces the hydrogen from the acid. The hydrogen passes off as a gas, and the zinc unites with the remainder of the acid molecule, forming what is called a *salt*. When the acid used

is hydrochloric acid, zinc chloride is the salt formed; when sulfuric acid is used, zinc sulfate is formed.

The reactions between iron, magnesium, and aluminum with each of these acids may be represented by the equations:



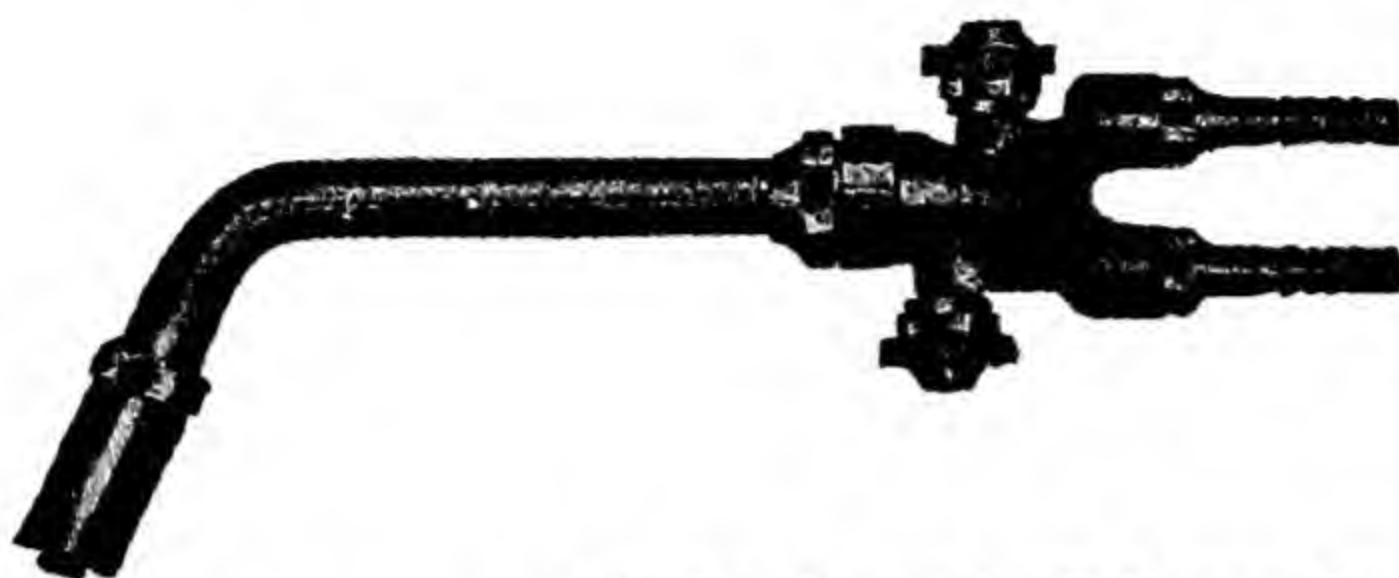
The formula equations for these reactions may be found on pages 141–143.

Physical properties of hydrogen. Hydrogen, like oxygen, is odorless, colorless, and tasteless. Since we are able to collect it over water, we know it is not very soluble in water. It is the lightest of all the elements. Air is about 14 times as heavy as hydrogen, and oxygen is 16 times as heavy. One liter of hydrogen weighs slightly less than 0.09 g. at 0°C. and under atmospheric pressure. At a very low temperature (−253°C.), hydrogen condenses to a liquid. At a still lower temperature it freezes, forming a crystalline solid.

Hydrogen gas molecules, like those of all other gases, are always in motion, colliding with each other and bombarding the sides of the container. Moreover, since hydrogen molecules are the lightest of all molecules, they move with greater speed than other gas molecules under the same conditions and scatter themselves, or *diffuse*, more rapidly than do any other gas molecules. If a glass bottle filled with hydrogen is inverted over a similar glass bottle filled with air, one would suppose that the hydrogen molecules would remain in the upper bottle, above the much heavier air. However, such is not the case. Within a few minutes many of the hydrogen molecules will have diffused into the lower bottle, and many of the heavier molecules of the air will be found mixed with hydrogen in the upper bottle. All gases diffuse in this way until a uniform mixture is produced.

Chemical properties of hydrogen. Hydrogen burns easily in oxygen or air, forming water. Pure hydrogen burns quietly, but a mixture of hydrogen and air explodes when ignited if the mixture is more than 10 per cent and less than 65 per cent hydrogen. Hydrogen can be burned in the same way that illuminating gas is burned. The hydrogen flame is almost invisible, and it is intensely hot. When hydrogen burns with pure oxygen, very high temperatures may be reached. The oxyhydrogen blowpipe

is a device for making use of this property. The hydrogen passes through the outer tube and is lighted at the tip. Then oxygen is turned on in the inner tube. Since the two gases are mixed just as they are leaving the mouth of the blowpipe, no explosion results.

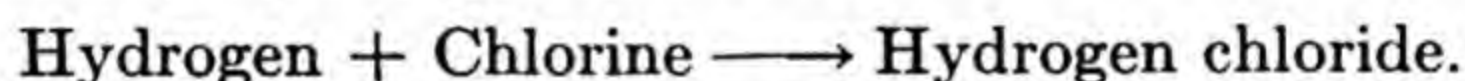


Courtesy, Braun-Knecht-Heimann Co.

Fig. 40. The oxyhydrogen blowpipe.

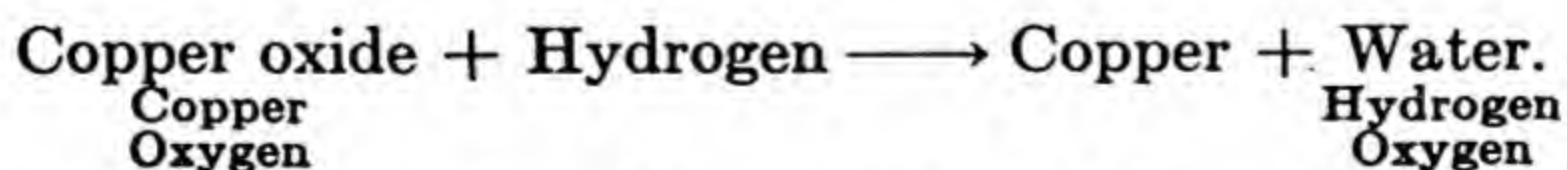
Hydrogen does not support combustion. When a lighted candle is inserted in a bottle of hydrogen, the candle flame goes out, but the hydrogen burns with an almost invisible flame at the mouth of the bottle. As the candle is withdrawn again, it becomes ignited by the burning hydrogen at the mouth of the bottle. The hydrogen burns only at the mouth of the bottle, where it is in contact with the oxygen of the air.

Besides burning in oxygen, hydrogen burns readily in the gas chlorine, forming hydrogen chloride:

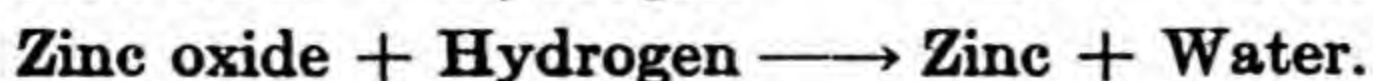
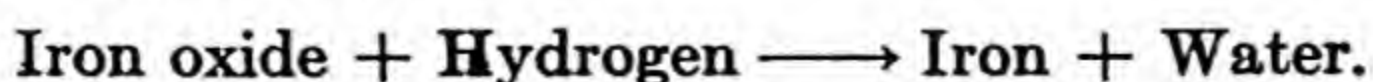


Under the proper conditions, hydrogen combines with nitrogen to form ammonia, with sulfur to form hydrogen sulfide, and with many metals to form hydrides.

Reducing action of hydrogen. Hydrogen has so great a tendency to combine with oxygen that it even takes the oxygen away from the metal in an oxide. When, for example, hydrogen gas is passed over hot copper oxide, free copper and water are formed. The water formed comes off as steam at the mouth of the tube:



A similar action occurs with hydrogen and iron oxide, or with hydrogen and zinc oxide:



The process of taking combined oxygen away from a substance is called *deoxidation*, which is one type of *reduction*. The hydrogen reduces the metal oxide to free metal. Hydrogen is called a *reducing agent*.

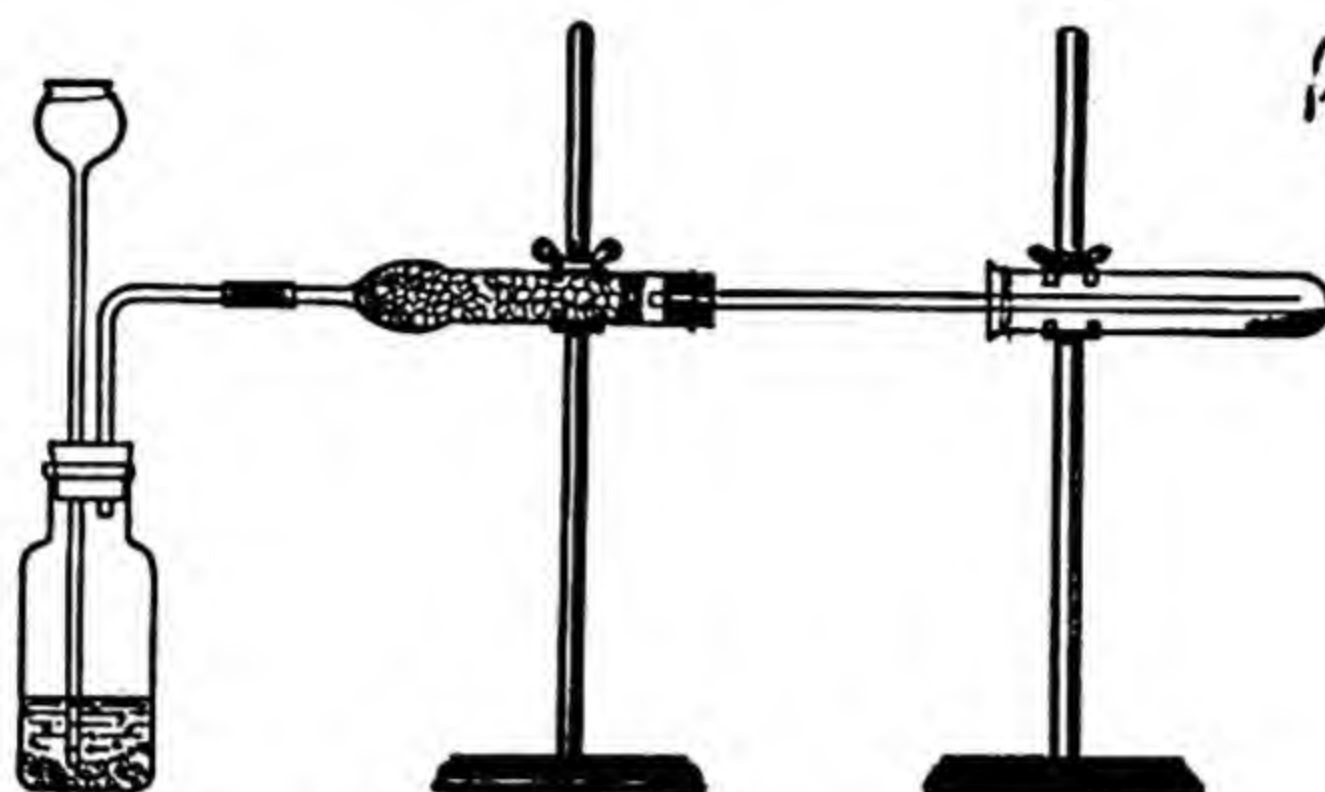
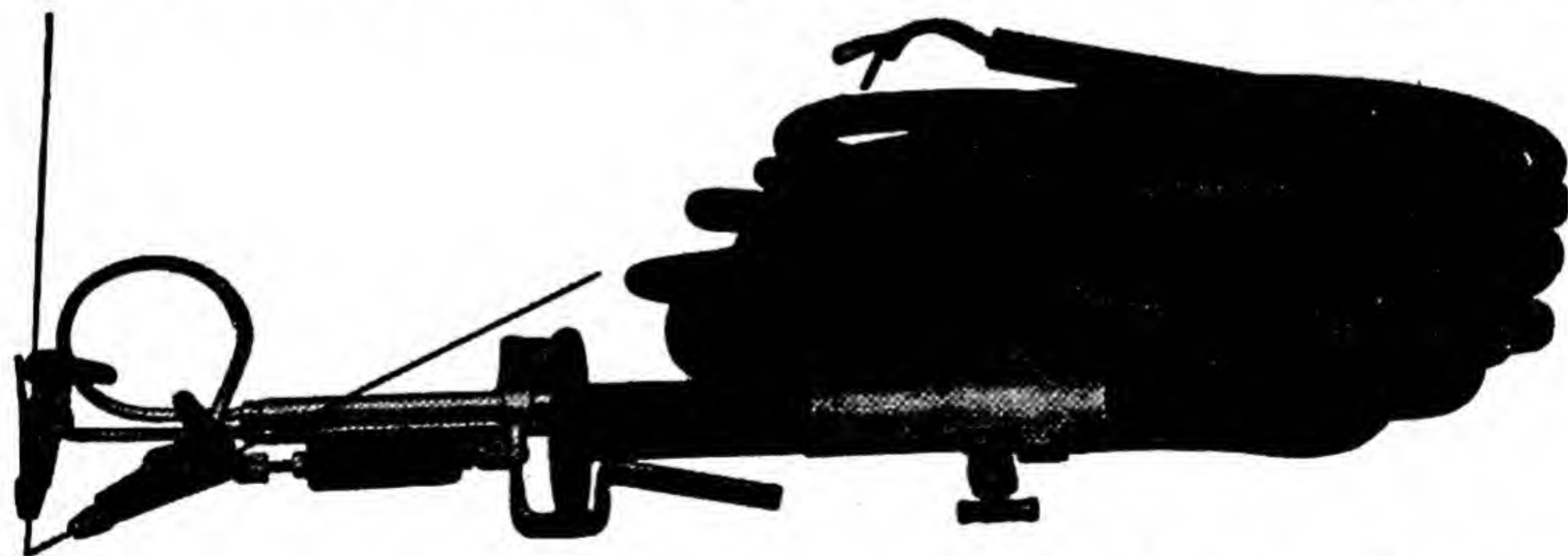


Fig. 41. Reduction of hot copper oxide by hydrogen.

Atomic hydrogen. We have learned that the hydrogen molecule is made up of two atoms of hydrogen firmly held together. A very large amount of energy is required to tear apart the two atoms. An electric arc is hot enough to break hydrogen molecules into hydrogen atoms, and when the atoms thus formed collide with each other and recombine, energy is given off in the form of heat. Hydrogen atoms colliding in space do not combine readily, but if



Courtesy, General Electric Co.

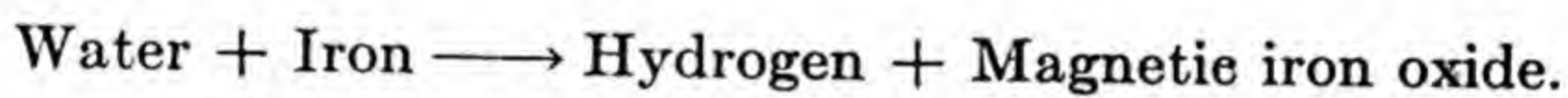
Fig. 42. The atomic hydrogen torch.

collisions between hydrogen atoms take place on a metallic surface, they combine immediately. A metallic surface is able to remove the energy which the atoms must give up before they can recombine. A commercial application of this principle is the atomic hydrogen torch developed by the General Electric Company. In this torch the hydrogen molecules are forced through an electric arc between tungsten electrodes and are

dissociated into atoms. A metal to be melted or welded provides the necessary surface for catalyzing the recombination of the atoms. The heat produced when the atoms recombine is sufficient to melt the metal. If air is present, additional heat is released as the hydrogen burns and forms water. All the common metals and alloys can be welded by the use of the atomic hydrogen torch.

Uses of hydrogen. There are many uses of hydrogen in addition to those already mentioned. It is used extensively as a fuel. As prepared for this purpose, it is usually mixed with other gases. Water gas is a mixture of hydrogen and carbon monoxide. Large amounts of hydrogen are used in the manufacture of methanol (wood alcohol) and in the production of ammonia, which is a compound composed of nitrogen and hydrogen. When hydrogen is bubbled through inexpensive liquid fats in the presence of a suitable catalyst, valuable fats, solid at ordinary temperatures, are produced. This process is called *hydrogenation*. Thousands of tons of these hardened fats are made each year, and find use as substitutes for lard and in the manufacture of soap and candles.

Reversible reactions: equilibrium. In our study of the methods for making hydrogen, we learned that when steam is passed over hot iron, hydrogen and magnetic iron oxide are produced:



We learned also that when hydrogen is passed over hot iron oxide, water and iron are produced. The second reaction is the reverse of the first one, and we say that the reaction between water and iron is *reversible*. When steam is passed in a steady stream through a tube containing iron, and the hydrogen is removed at the outlet of the tube, all of the iron is changed gradually to iron oxide. We then say that the reaction has "gone to an end" or "gone to completion." Conversely, if a stream of hydrogen is passed through a tube containing iron oxide, the oxygen is removed from the iron oxide by the hydrogen, and water vapor is formed, escaping from the outlet of the tube. During this process, all of the iron oxide may be reduced to iron. Again the reaction goes to an end.

Let us see what takes place when we heat iron and steam in a closed container. A reaction can occur only when the steam and iron molecules come in contact with each other. Since the molecules of steam are in rapid motion, some of them strike the surface of the iron. The iron removes oxygen from the steam (hydrogen oxide), forming iron oxide and liberating hydrogen. At the beginning of the experiment when there are a great many

molecules of steam present, the reaction takes place rapidly, since many collisions occur between the hydrogen oxide molecules and the iron. The reaction becomes slower as the number of steam molecules decreases.

The amount of hydrogen and iron oxide is continually increasing during the process. When hydrogen molecules strike the iron oxide which has been formed, they reduce the oxide to iron, and become steam molecules. As the number of hydrogen and iron oxide molecules increases, the frequency of their collisions also increases; so the reaction goes faster and faster. Finally a condition is reached in which hydrogen is reducing iron oxide at the same rate that iron is reducing hydrogen oxide, and we say that

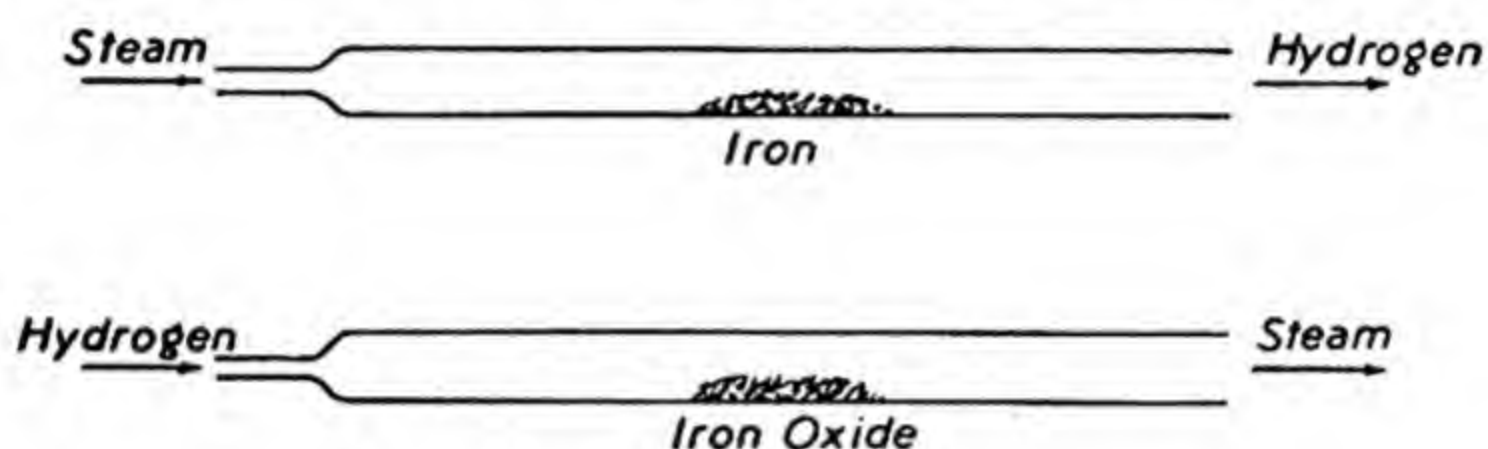
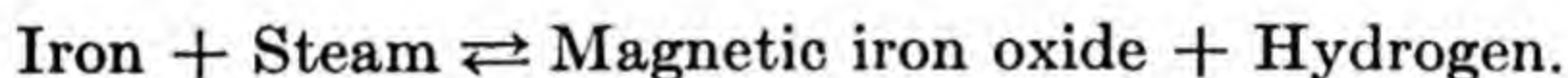


Fig. 43. A reversible process.

the reactions are in a state of *equilibrium*. All four substances are present in the container at *equilibrium*. We often use arrows pointing both ways to show that a reaction is reversible:



If we desire to cause such a reversible reaction to go to an end, we must remove at least one product of the reaction as fast as it is formed. A volatile product is easily removed by allowing it to escape. When a gas is formed during a reaction carried out in the laboratory, the gas is allowed to escape into the air, or it is caught in bottles and removed. Removal of a product of either reaction prevents the attainment of equilibrium, and the reaction goes to an end. We shall find later that reactions in which one of the products is an insoluble substance also go to an end.

Isotopes. The hydrogen atom is the smallest and lightest of all known atoms. We find, however, that not all atoms of hydrogen are exactly alike. In 1932 it was discovered that there are some hydrogen atoms (about 1 in every 5000) that are twice as heavy as the ordinary hydrogen atom. These were, at first, called "heavy hydrogen" atoms, and the gas formed by the union of two such atoms was called heavy hydrogen gas. We now use the name *deuterium* for this kind of hydrogen, and we speak of "deuterium atoms" and "deuterium gas." This gas and ordinary hydrogen have the same *chemical* properties; hence they are two

forms of the same element. The deuterium atom is an *isotope* of the light hydrogen atom.

A still heavier hydrogen atom, one that weighs three times as much as the light one, was discovered in 1937. We shall find that there are isotopes of many elements, including oxygen, nitrogen, lead, sodium, and tin.

Questions and Exercises

1. Describe the physical properties of hydrogen.
2. What property of hydrogen makes it valuable for inflating balloons?
3. What property of hydrogen makes it undesirable for use in balloons?
4. Why is smoking not permitted on board a dirigible filled with hydrogen?
5. How could you distinguish between a jar filled with hydrogen and one filled with air?
6. Sugar, starch, and cellulose are compounds containing hydrogen. These compounds are produced by growing plants. From what source do you suppose plants obtain the necessary hydrogen?
7. Is there hydrogen in the air? If so, why does the atmosphere not explode when a match is lighted?
8. Name five compounds that contain hydrogen.
9. Outline two methods for making hydrogen gas, and make a sketch of the apparatus required for each process.
10. What is deoxidation?
11. Give an example of a deoxidation process, and describe in a general way the changes that take place between the molecules in the process.
12. Describe the process of welding by the atomic hydrogen torch. What is the source of heat in this process?
13. In an ordinary hydrogen torch, hydrogen gas is mixed with air and burned. Describe the chemical change that supplies the welding heat in this case.
14. Why is it incorrect to say that all atoms of the same element are alike in all respects?
15. If the "lifting power" of a balloon is the difference between the weight of the gas in the balloon and that of the same volume of air, what is the lifting power of a balloon using 10,000 liters of hydrogen?
16. What results would you expect if a lighted candle were thrust into: (a) a bottle of hydrogen, (b) a bottle of a mixture of air and hydrogen, (c) a bottle of oxygen, (d) a bottle of air from which the oxygen has been removed?
17. Name three substances found in the home which contain hydrogen.
18. How would a soap bubble behave if filled with hydrogen instead of air?
19. Two toy balloons are filled with gas, the first with hydrogen and the second with natural gas (a compound of carbon and hydrogen). Which balloon will first become deflated? Explain.
20. If an unstoppered bottle filled with hydrogen gas is left standing inverted on a table overnight, will the bottle still be filled with hydrogen in the morning?

PART 4

Water; Hydrogen Peroxide

Water

Water is the most abundant of all chemical compounds on the surface of the earth. The total surface of the globe is about 197,000,000 sq. mi., and of this approximately 71 per cent, or 140,000,000 sq. mi., is water. This area includes the water in the



Courtesy, Horace D. Lyon, Carmel

Fig. 44. More than 70 per cent of the surface of the earth is water.

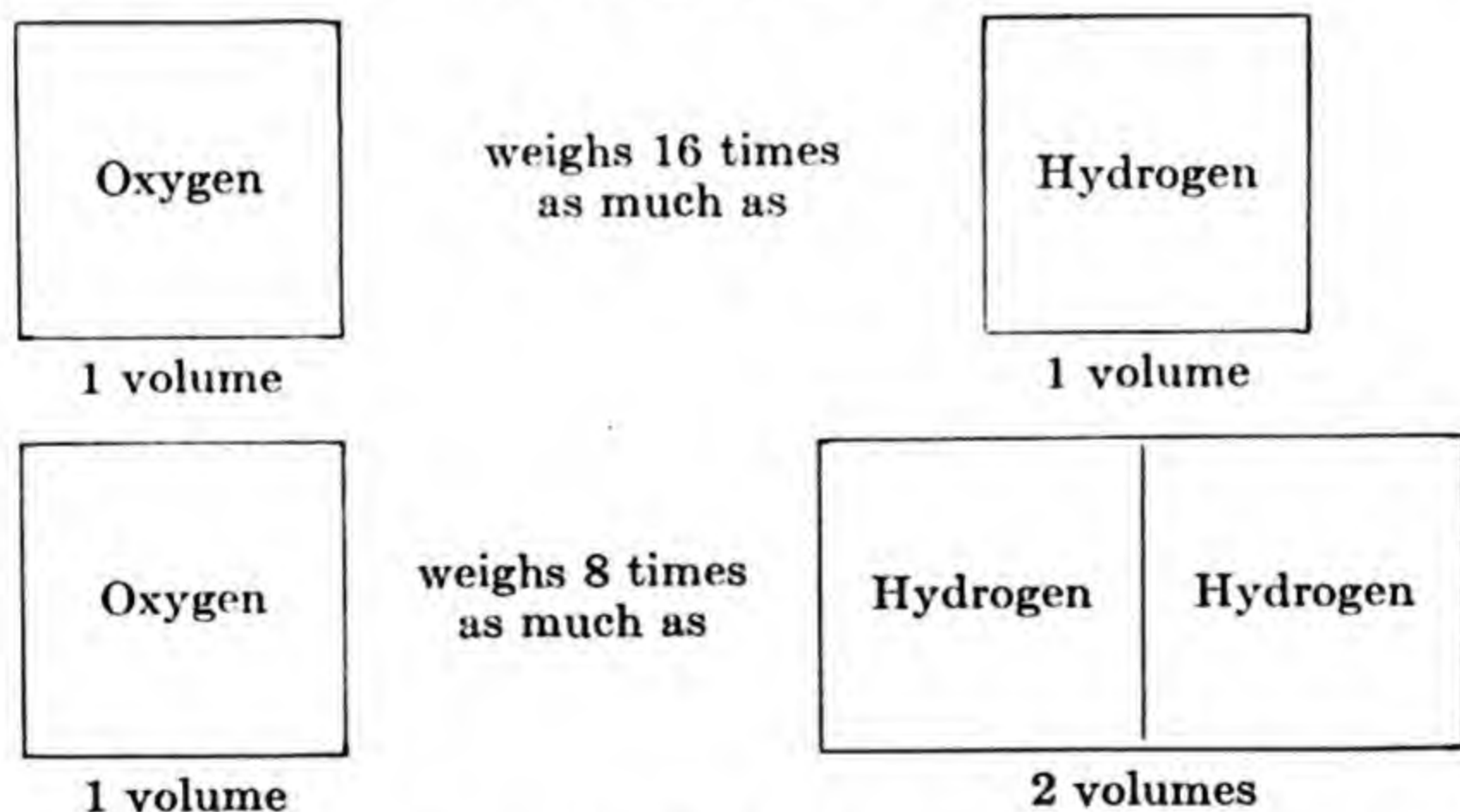
oceans, in the lakes, in the rivers, and in the streams. In addition, water exists in the crust of the earth. In many places there are large streams of underground, or artesian, water. When we bore a well, we hope to strike this artesian water. Underground streams are sometimes under pressure, and the water is forced through crevices in the rocks, forming springs. Almost everything contains at least a trace of water. A piece of coal or chalk or a sample of dust

from the road, if heated, will lose weight on account of the escape of moisture.

Water is essential to life, and it constitutes more than 50 per cent by weight of every living plant and animal. Our bodies are approximately 70 per cent water. Many of the foods we eat are composed primarily of water. Tomatoes are 95 per cent; milk, 87 per cent; beef, from 60 to 68 per cent water.

Analysis of water. When we electrolyze water, we find that it yields two volumes of hydrogen for every volume of oxygen. The process of discovering what a compound is made of, by separating it into the elements of which it is composed, is called *analysis*. When a boy dismantles a clock to see how it works, he is, in a way, analyzing it.

If we were to weigh the hydrogen and oxygen liberated in the electrolysis of water, we should find that the oxygen actually weighs 8 times as much as the hydrogen, although its volume is only half as great. This difference is explained by the fact that oxygen is heavier than hydrogen. Any volume of oxygen weighs 16 times as much as the same volume of hydrogen.



We know, then, by analysis that the ratio of the hydrogen to the oxygen in water is 2 to 1, by volume; and the ratio is 1 to 8, by weight.

The composition of water illustrates the *law of definite proportions*. Every chemical compound always contains the elements of which it is composed in exactly the same proportions. The composition of water is always one-third oxygen and two-thirds hydrogen, by volume; or eight-ninths oxygen and one-ninth hydrogen, by weight. Every sample of sodium chloride, no matter from what source it is obtained, is composed of 23 parts of sodium to 35.5 parts of chlorine, by weight. In other words, *a chemical compound has a definite composition*.

Synthesis of water. After a boy has torn his clock to pieces, he may begin to reassemble the parts. If he is successful in placing them in their proper positions, he has built a clock having all the properties of the original one. The chemist, likewise, is not satisfied with merely analyzing substances in order to determine how they are built. He must also synthesize them. The *synthesis* of a compound consists in making it from its elements. Water is easily synthesized by burning hydrogen in an atmosphere of oxygen. The apparatus for this experiment is shown in Fig. 45. Measured volumes of hydrogen and oxygen are mixed in the tube. Platinum wires sealed in the glass lead to an induction coil, which can be used to produce a spark in the gap between the wires in the tube. The spark ignites the mixture of hydrogen and oxygen, causing an explosion. A mist of water vapor, which soon condenses to liquid water, appears in the tube, and the mercury rises to a higher level. When the gas mixture is composed of exactly twice as much hydrogen as oxygen, by volume, no gas remains in the tube after the explosion, and the mercury rises until it fills the tube. (The volume of liquid water formed in the explosion is negligible.) If 20 cc. (cubic centimeters) of hydrogen gas is mixed with 15 cc. of oxygen and ignited, a residue of 5 cc. of oxygen remains in the tube after the reaction is completed. If an excess of hydrogen were used, for example, a gas mixture of 30 cc. of hydrogen and 10 cc. of oxygen, we should find that 10 cc. of hydrogen remained in the tube after the explosion occurred. We are able, therefore, to prove by synthesis as well as by analysis that water is made of hydrogen and oxygen in the proportion of 2 to 1, by volume.

When the tube in which the explosion occurs is surrounded by a steam jacket so that the water formed cannot condense, but remains in the form of steam, or gaseous water, we find that the volume of the steam formed is exactly the same as the volume of hydrogen used. Hence, two volumes of hydrogen combine with one volume of oxygen to form two volumes of steam.

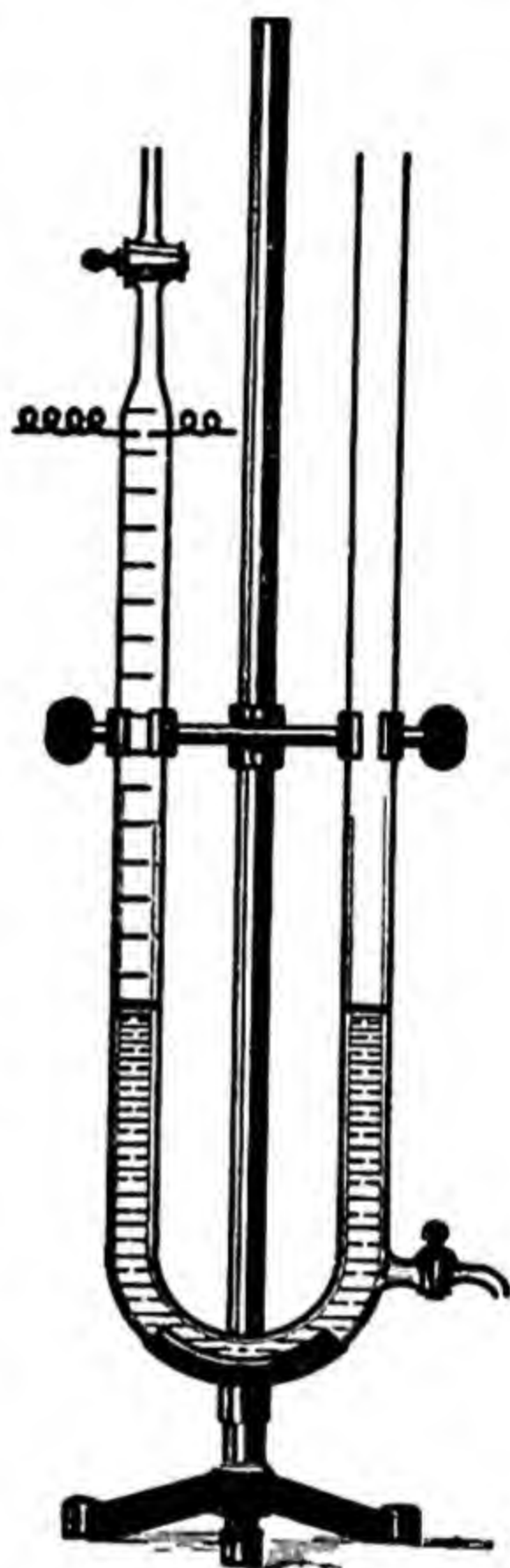
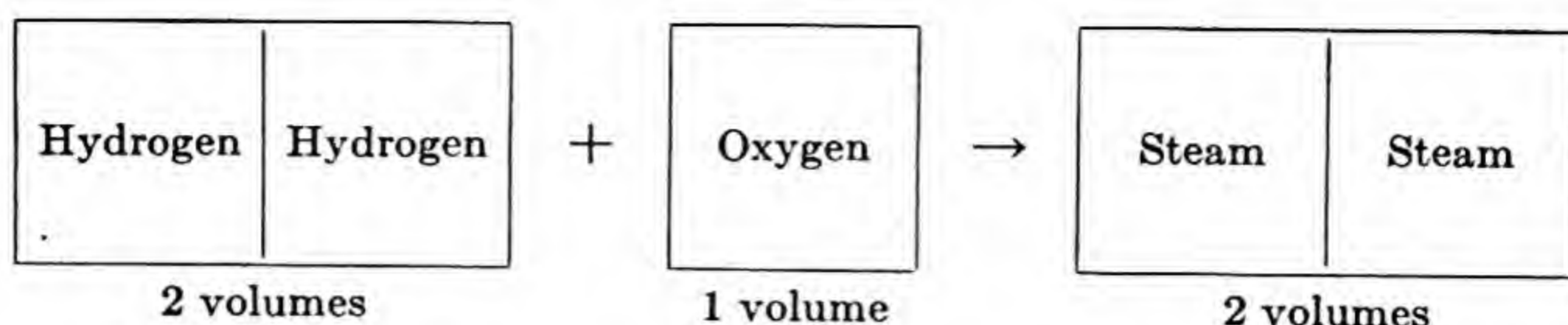


Fig. 45. Measured volumes of hydrogen and oxygen are mixed and exploded. Two volumes of hydrogen combine with one volume of oxygen, forming water.



When we wish to determine the relative weights of hydrogen and oxygen by synthesizing water, we may use the method illustrated by Fig. 46.

A porcelain boat filled with dry copper oxide is weighed and placed in a hard glass tube *B*. The U-tubes *C* and *D*, containing enough concentrated sulfuric acid to seal the bends of the tubes, are attached as shown in the figure.

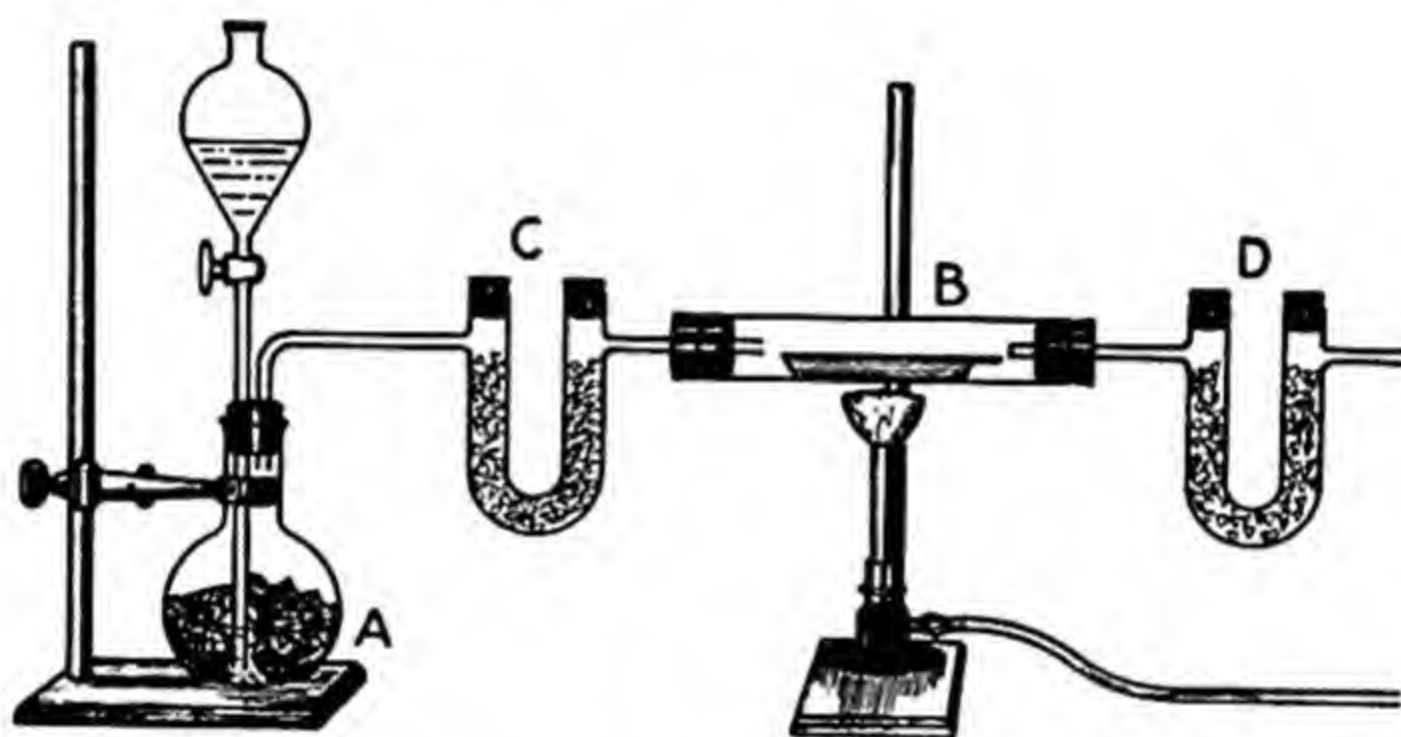
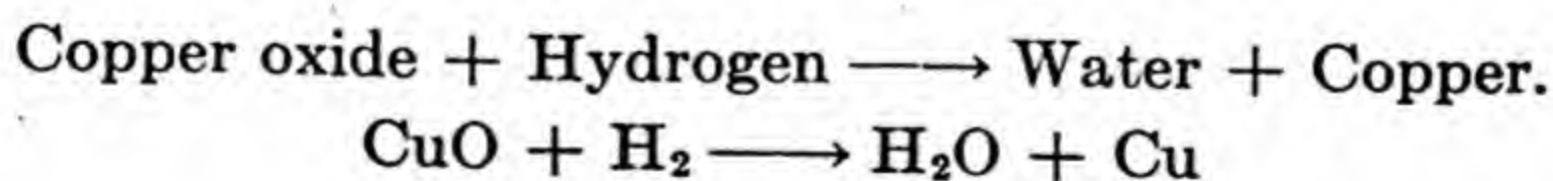


Fig. 46. Hydrogen gas is passed over hot copper oxide. The water formed is collected in sulfuric acid and weighed.

The U-tubes are generally filled with glass beads moistened with sulfuric acid. The beads increase the surface of the acid exposed to the water vapor, making the apparatus more efficient in absorbing water. Hydrogen gas is generated in the flask *A* and dried by passing it through the U-tube *C*. The dry hydrogen gas then passes over the copper oxide, which is heated with a gas flame. The hydrogen gas reacts with the hot copper oxide, forming water and copper as indicated by the following equations:



The water formed in the reaction is absorbed in the U-tube *C*, and the gain in weight of this tube represents the weight of water formed. The loss in weight of the contents of the porcelain boat represents the weight of oxygen used. The difference between the weight of water formed and the weight of oxygen used is the weight

of hydrogen consumed in forming the water. One experiment of this kind supplied the following data:

	<i>Grams</i>
Original weight of boat and CuO.....	45.7
Final weight of boat and its contents.....	42.5
Difference = weight of oxygen used.....	3.2
Original weight of U-tube and H ₂ SO ₄	73.2
Final weight of U-tube and contents.....	76.8
Difference = weight of water formed.....	3.6

Weight of hydrogen in 3.6 g. of water = $3.6 - 3.2 = 0.4$ g.

$$\text{Ratio of hydrogen to oxygen in water} = \frac{0.4}{3.2} = \frac{1}{8}$$

Properties of water. Pure water is odorless and tasteless. The taste and odor of natural water are due to dissolved gases and minerals. Distilled water, from which all dissolved substances have been removed, tastes "flat." In shallow containers water is colorless, but deep water is blue. Under atmospheric pressure, at sea level, water boils at 100°C. (212°F.) and freezes at 0°C. (32°F.)

If we gradually cool a beaker of warm water, its volume becomes smaller and smaller until a temperature of 4°C. is reached. In other words, the water becomes more and more dense as its temperature approaches 4°C. Then, as the temperature is further lowered, the volume increases—the water becomes less dense. Liquid water is heavier at 4°C. than at any other temperature; or, as it is usually stated, liquid water has its greatest density at 4°C. At this temperature 1 cc. of water weighs exactly 1 g. As the temperature is lowered still more, the water continues to expand until, at 0°C., the liquid water changes to ice. The volume of ice is still greater than that of the same weight of water at 0°C.; that is, ice is less dense than liquid water, and it floats. The bursting of water pipes in winter is due to this expansion when water solidifies. Water which has seeped into crevices in rocks may split huge boulders because of the great force exerted by the expansion of the water during the formation of ice.

Alcohol, chloroform, benzene, gasoline, and nearly all liquids except water continue to contract as they approach their freezing points, and they contract also during the process of crystallizing. When they freeze, the crystals sink to the bottom of the container. If water behaved in this way, the ice formed in lakes and rivers would settle to the bottom and the entire volume of water might become solid. Fish and other forms of aquatic life would not survive under these conditions.

Vapor pressure. We have all observed that water evaporates from an open dish, that is, that some of the molecules of liquid water change into the gaseous state and escape into the air. As the evaporation continues, the temperature of the water in the dish gradually drops, unless the water obtains heat from some outside source. In a liquid the molecules are in constant motion, their speed being dependent upon the amount of heat energy they possess. As the molecules collide with each other some of them acquire more energy than the average, and others are left with less than the average amount of energy. Some of the most rapidly moving molecules (those having more than average energy) escape from the surface of the liquid. This removal of molecules high in heat energy leaves the liquid with a lower heat content, and the liquid becomes cooler. The temperature of a substance is a measure of the average heat content of its molecules.

When a liquid is placed in a closed container, the molecules having the most energy, and hence the greatest speeds, escape into the space above the liquid, but they are not free to diffuse into the surrounding atmosphere. These gas molecules are in motion and some of them, striking the surface of the liquid, return to the liquid state. When the rate at which molecules escape from the liquid is equal to the rate at which molecules return to the liquid, a state of balance, or equilibrium, is reached. The space above the liquid is then said to be saturated with the gas or vapor molecules. The liquid, in this case, does not become cooler, since rapidly moving molecules return to the liquid at the same rate that similar molecules escape from the liquid.

When a liquid is heated, the average speed of all its molecules is increased. This increase causes more molecules to acquire enough energy to escape from the surface and go into the gaseous state, and the liquid evaporates more rapidly. In a closed container, a new state of equilibrium is reached at the higher temperature with more molecules in the gaseous state than there were at the lower temperature.

The amount of vapor in equilibrium with the liquid may be expressed in a number of ways. It may be stated as the number of gaseous molecules per unit volume of the vapor, or it may be specified as the weight of vapor in a known volume, for example, one liter. Since the vapor acts like any other gas, exerting a pressure on the walls of the container, it is convenient to express the state of equilibrium in terms of the pressure produced by the molecules. Gas pressure is usually measured by the height of a column of mercury, which just balances the pressure exerted by the gas. The height of the column of mercury in a barometer meas-

ures the pressure of the gases in the atmosphere. The vapor pressure of a liquid is the pressure exerted by its vapor when in equilibrium with the liquid.

The change of vapor pressure of a liquid, with the temperature, is shown for several liquids in Fig. 47. When the liquid is heated in an open vessel to the point at which the vapor pressure is equal to the pressure of the atmosphere, bubbles of vapor appear and the liquid passes rapidly into the gaseous state. We say that the liquid is boiling. The *boiling point* of a liquid is defined as the

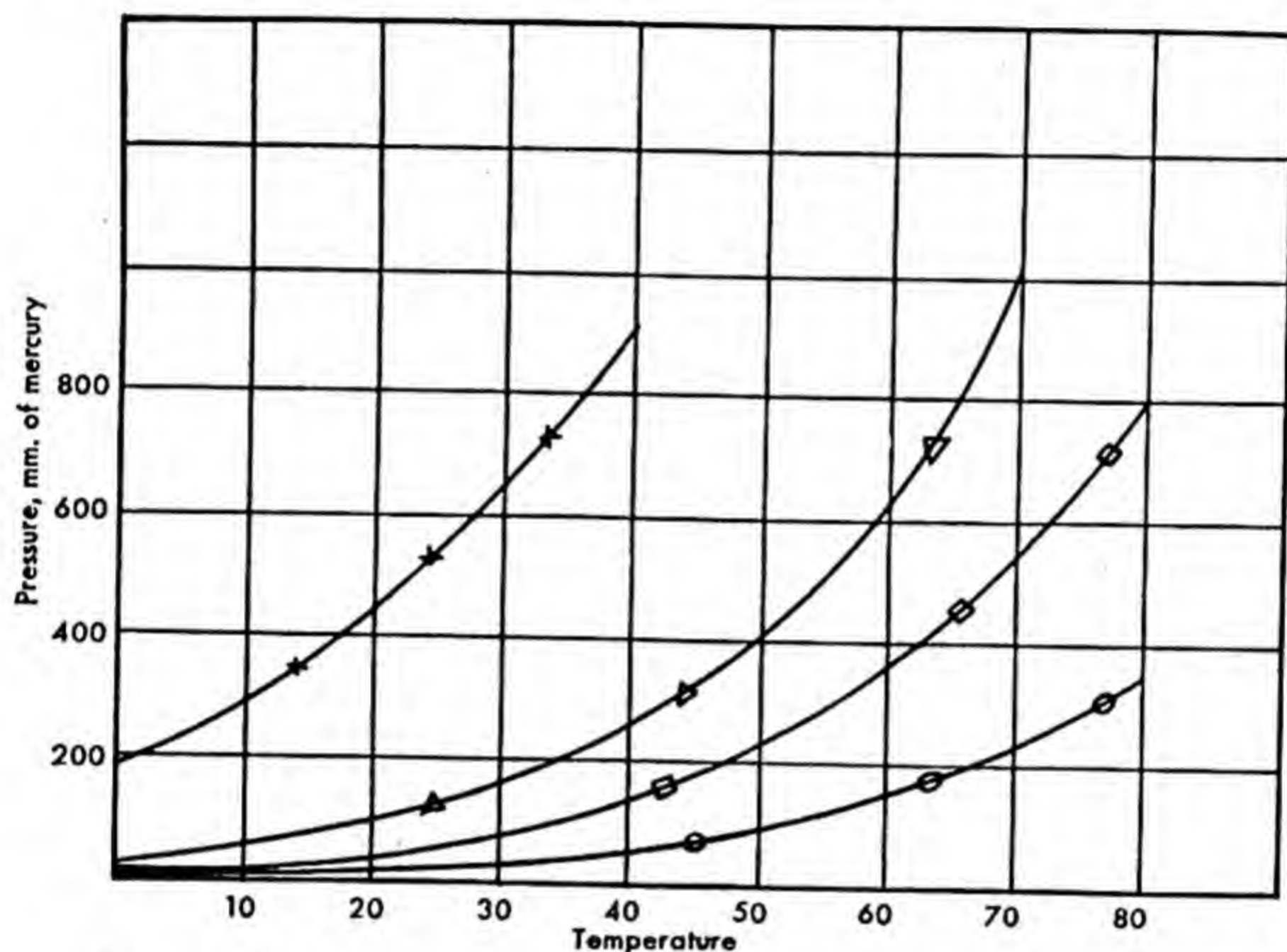


Fig. 47. The vapor pressures of several common liquids at various temperatures.

× Ether

Δ Methyl alcohol

□ Ethyl alcohol

○ Water

temperature at which the pressure of the vapor, in equilibrium with the liquid, is equal to one atmosphere.

Many solids, also, are in equilibrium with their own vapors. The vapor pressures of ice have been measured at several temperatures. Much of the snow which falls in the winter evaporates into the air, without first going through the process of melting. The direct change of a solid to a vapor, without passing through an intermediate liquid state, is called sublimation.

Heat of vaporization. When pure water is heated, the temperature gradually rises until it reaches 100°C . It requires 1 cal. (calorie) of heat to raise each gram of water 1° in temperature. A calorie is defined as the amount of heat required to raise the temperature of 1 g. of water through 1°C . If there are

100 g. of water in one container, 100 cal. will be absorbed by the water when the temperature goes up 1°C . If the 100 g. of water are heated from 20°C . to 100°C ., or through 80° , then 8000 cal. (that is, 80×100) of heat will be absorbed. At 100°C . water begins to boil if it is in a vessel open to the atmosphere, and it continues to boil as long as heat is applied. The temperature remains at 100°C ., although we can readily see that heat is continually being given to the water. Also, at 100°C ., steam or gaseous water passes off from the surface of the liquid, or bubbles of steam may form at the bottom of the container, pass up through the liquid, and escape at the surface.

Increasing the size of the flame under an open vessel does not raise the temperature of the boiling water. The rate of evaporation is increased by making the water boil more vigorously, but the temperature remains constant. Vegetables and meats do not cook any faster in rapidly boiling water than in slowly boiling water. Where, then, does the heat from the burner go if the temperature of the water does not increase?

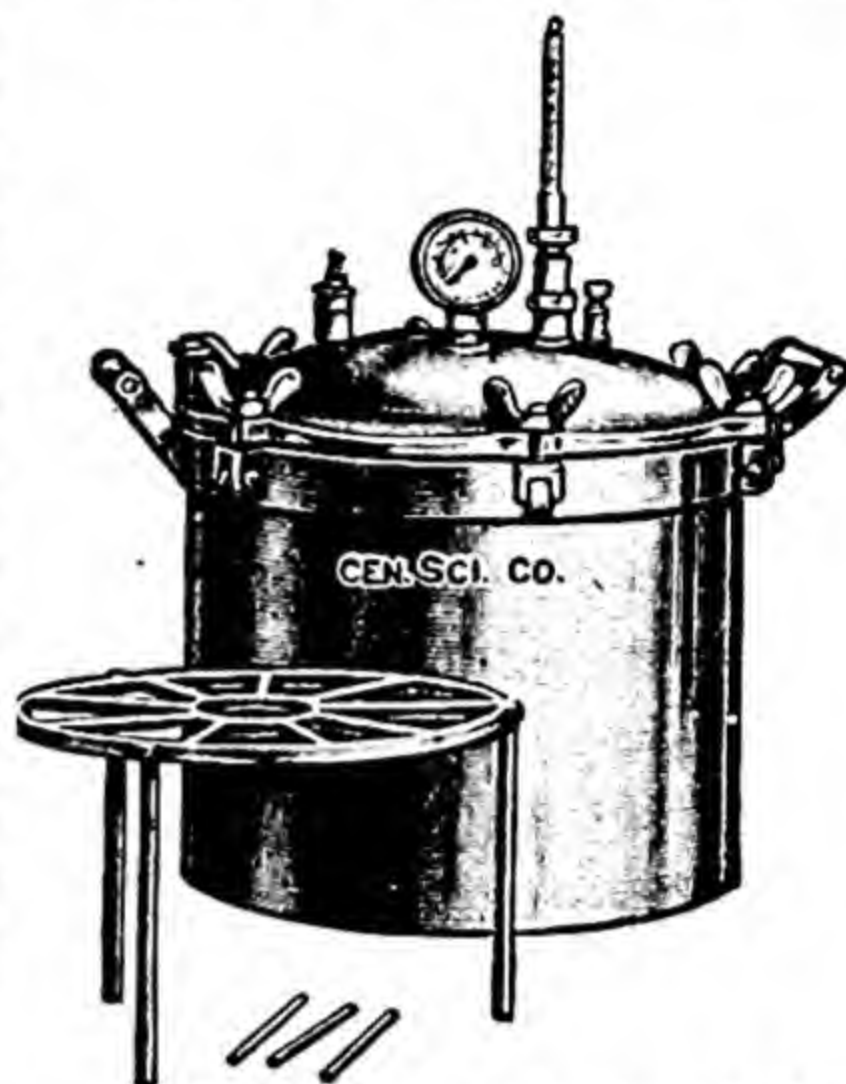
The molecules in liquid water are held together by a powerful cohesive force. In addition to this cohesion, the weight of the atmosphere on the surface of the liquid tends to prevent the escape of water molecules into the air. A molecule must acquire a tremendous amount of energy in order to break away from the liquid as a gaseous molecule. The flame supplies the necessary energy in the form of heat. It is found by experiment that 539 cal. of heat are absorbed by each gram of liquid water at 100°C ., in changing to water vapor at the same temperature. This quantity of heat is called the *heat of vaporization* of water. Every liquid requires a definite amount of heat to change it from a liquid to a gas, although the temperature of the gas is the same as the temperature of the liquid from which the gas was formed. The amount of heat required is different for every liquid, and hence is a property of the liquid.

When steam is cooled so that it condenses again to water exactly the same amount of heat is given off as was absorbed in the reverse process. In other words, when 1 g. of steam at 100°C . changes to water at 100°C ., 539 cal. of heat are given out.

We make use of this principle in our steam radiators used for heating buildings. Water is changed to steam in a large boiler, from which it is conveyed by insulated pipes to the radiator. The steam gives up its heat to the cooler air of the room, 539 cal. for every gram of steam used, and the water passes out at the bottom of the radiator, making room for more steam to enter from the boiler.

If water is heated in a closed container so that the vapor is not permitted to escape freely, it no longer boils at 100°C . It must be heated to a higher temperature in order that the molecules in the liquid state may acquire sufficient energy to overcome a pressure, which in this case is greater than that of the atmosphere. In steam locomotives, heat is applied and the escape of vapor is prevented until the water and the vapor above it reach a temperature in the neighborhood of 200°C . The steam then exerts sufficient pressure to accomplish the work of moving a train. When water is heated in a closed chamber until its temperature reaches 180°C ., the vapor above the water exerts a pressure of about 150 lb. per sq. in.

If, on the other hand, the pressure on the surface of water is less than atmospheric pressure, as it is at high altitudes or when some of the gas has been removed by means of a suction pump, water boils below 100°C . At the summit of Mt. Shasta (altitude 14,161 ft.), water boils at 90°C . Water which is boiling



Courtesy, Central Scientific Co.

Fig. 48. An autoclave or pressure cooker.

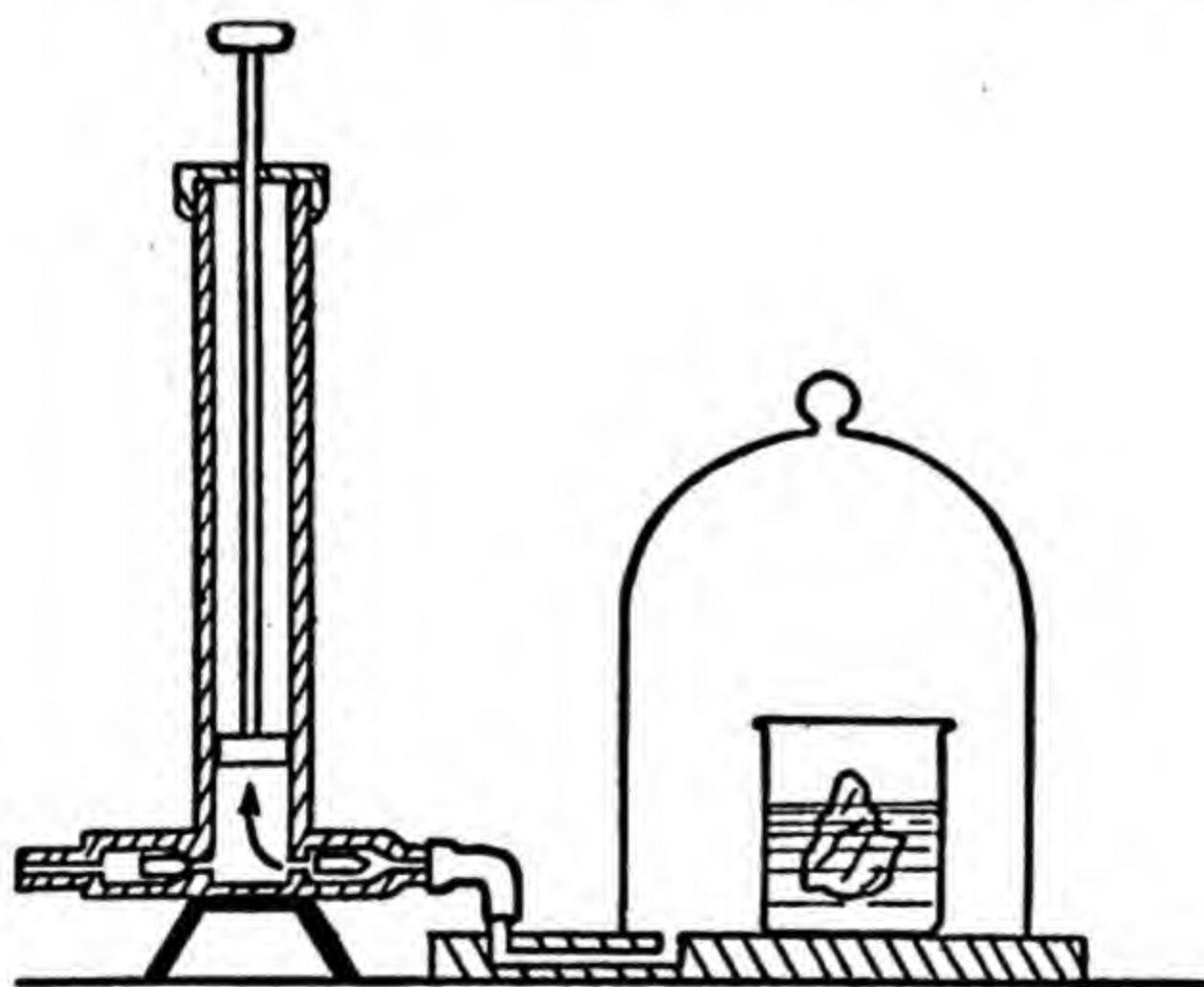


Fig. 49. Water freezes and boils at the same temperature if the pressure of the air and water vapor in the closed container is reduced to 4.6 mm.

at high altitudes is not as hot as at sea level; therefore a considerably longer time is required to cook foods by boiling at these higher altitudes. A pressure cooker is often used to overcome this

difficulty. A pressure cooker, or autoclave, is a vessel having a cover firmly clamped in place to prevent the escape of steam. The confined steam raises the pressure on the surface of the liquid far above that of the outside air. A higher temperature is then required to make the liquid boil, and the time required for cooking substances is reduced.

By means of a suction pump the pressure over a liquid may be lowered to such a degree that the liquid will boil at room temperature or even at lower temperatures. Boiling under reduced pressure is employed in the manufacture of sugar. If the water were boiled from the sugar solutions under atmospheric pressure, the sugar would be partially burned at the temperature necessary for the evaporation. The sugar solution is placed in large vacuum pans, and the pressure above the surface of the solution is kept below atmospheric pressure, by means of air pumps. The evaporation is carried on at a temperature so low that the sugar is not injured during the process.

Heat of fusion. If a beaker of water is gradually cooled, every gram of water gives off 1 cal. of heat for each degree the temperature drops. When the temperature has reached $0^{\circ}\text{C}.$, ice begins to form in the beaker. If we continue to remove heat from the water, the temperature remains at $0^{\circ}\text{C}.$, and more and more water changes to ice until it is completely solidified. During this process of solidification, 79 cal. of heat are given out by every gram of water at $0^{\circ}\text{C}.$, as it changes to ice likewise at $0^{\circ}\text{C}.$

Conversely, if we place some ice in a beaker and heat it *slowly*, with constant stirring, the ice will melt but the temperature of the mixture of ice and water will not rise above $0^{\circ}\text{C}.$ as long as ice is present. This temperature is the melting point of ice. The melting point of a solid may be defined as the temperature at which the solid and liquid states are in equilibrium, under a pressure of one atmosphere. In this process we continually add heat to the contents of the beaker without affecting the temperature in any way. The energy absorbed by the ice is used in tearing the molecules from the rather rigid positions which they occupy in the solid state and allowing them to move about as they do in liquid water. Every gram of ice at $0^{\circ}\text{C}.$ in melting to water at $0^{\circ}\text{C}.$ absorbs 79 cal. of heat. This is called the *heat of fusion* of ice. Our ice refrigerators are built on this principle. Ice is placed in a box, the sides of which are packed with cork or other material which does not conduct heat rapidly from the outer air to the interior of the refrigerator. Food at room temperature is placed in the ice box and the ice, as it melts, takes heat from its surroundings. Every gram of ice, in melting, takes 79 cal. of heat from the

food, soon reducing the temperature of the food to the neighborhood of 0°C .

Heavy water. It has been discovered that approximately one molecule of water in every 5000 is different from the water molecules which we have been discussing. This kind of molecule is composed of two atoms of heavy hydrogen, or deuterium, combined with one atom of oxygen. This kind of water is called "heavy water," or better, deuterium oxide. Considerable amounts of these heavy molecules have been separated from the ordinary light ones, and their properties have been studied. Heavy water boils at 101°C . under atmospheric pressure at sea level. Ordinary water boils at 100°C . under the same conditions. One cubic centimeter of deuterium oxide weighs 1.107 g.

Natural waters. Pure water is never found in nature. Water dissolves almost everything with which it comes in contact. Even rocks are slightly soluble in water. Rain water is probably the purest form of natural water, but it contains dissolved gases and dust. The rain and snow that fall over a large city may be quite impure. We have all observed that the air is often clear after a rain, and that we can see things at great distances. That is because the rain has removed the dust and smoke from the air. The purest form of rain falls over the ocean, but even this rain has oxygen, nitrogen, and carbon dioxide dissolved in it.

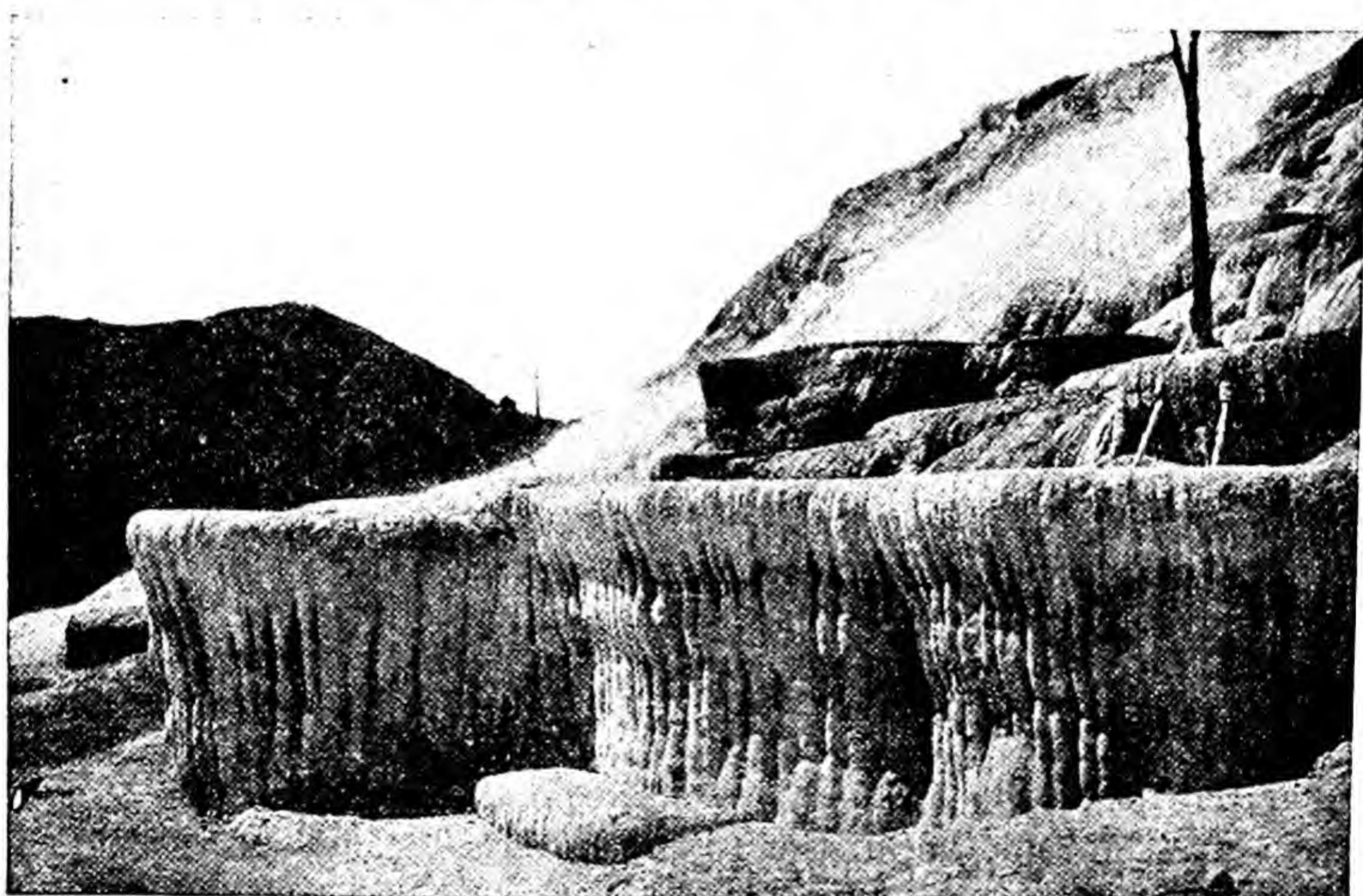
Mountain lakes which are formed from melting snow and from springs are comparatively pure, but they contain dissolved gases and minerals with which the water has come in contact. There is usually decaying plant material also in the bottom of such lakes, which adds impurities to the water.

Spring water may be relatively pure, or the water which issues from the earth in this form may be so heavily charged with dissolved substances that it is called mineral water and the sources are called mineral springs. Compounds of iron, silicon, calcium, magnesium, and sulfur are among the dissolved substances found in many of these mineral springs. Some which contain large amounts of carbon dioxide are called "soda springs." Volcanic country is usually rich in mineral springs.

Rivers contain dissolved or suspended particles derived from the soil. Rain water may find its way to a river by percolating through the soil or by flowing over the surface of the land. In either case it dissolves the more soluble minerals of the earth with which it comes in contact. River water contains also products of decomposing plant material. A rapidly flowing stream carries clay and small bits of sand and rock in suspension. The ocean contains a greater variety of dissolved and suspended

substances than any other natural water. It is salty because for thousands of years rivers have carried to it their small loads of soluble substances.

Water is continually being evaporated from the surface of the ocean. The pure water vapor is carried by air currents back over the land to be precipitated again as rain or snow. It then begins its journey once more toward the sea and gathers on its way another load of soluble materials. This process has been repeated millions of times since our earth was formed, so that it is not surprising to



Courtesy, J. E. Haynes Picture Shop

Fig. 50. Travertine (calcium carbonate) deposits from mineral springs. Mammoth Hot Springs, Yellowstone National Park.

find that the ocean contains large quantities of dissolved substances. Sea water contains on the average about $3\frac{1}{2}$ lb. of salty material in every 100 lb. of water. About $2\frac{1}{2}$ lb. is sodium chloride. The Dead Sea, Great Salt Lake, and many smaller bodies of water have become saturated with salt. Five barrels of water taken from Great Salt Lake yield one barrel of salt.

The purification of water. Pure water can be made from any of the natural waters by distillation. Distillation consists in changing a liquid to a vapor at the boiling point, and then cooling the vapor below the boiling point so that it again becomes a liquid. The substances dissolved in the water, such as salt, and suspended matter like particles of clay and bacteria, do not form a vapor but

remain in the distilling flask. Hence the water which has been distilled is obtained free from dissolved and suspended solids. It still contains any gaseous impurities which were dissolved in the water. These are usually carried off in the first portion of water that distills over, so if this portion is discarded, the remainder of the distillate will be free from gaseous impurities.

The apparatus used for small-scale distillation is shown in Fig. 51. Water in the distilling flask is heated to boiling. The vapor passes through the inner tube of the condenser. It is cooled by a stream of water which flows between the two tubes of the condenser. The vapor liquefies in the condenser and is collected in the receiving flask.

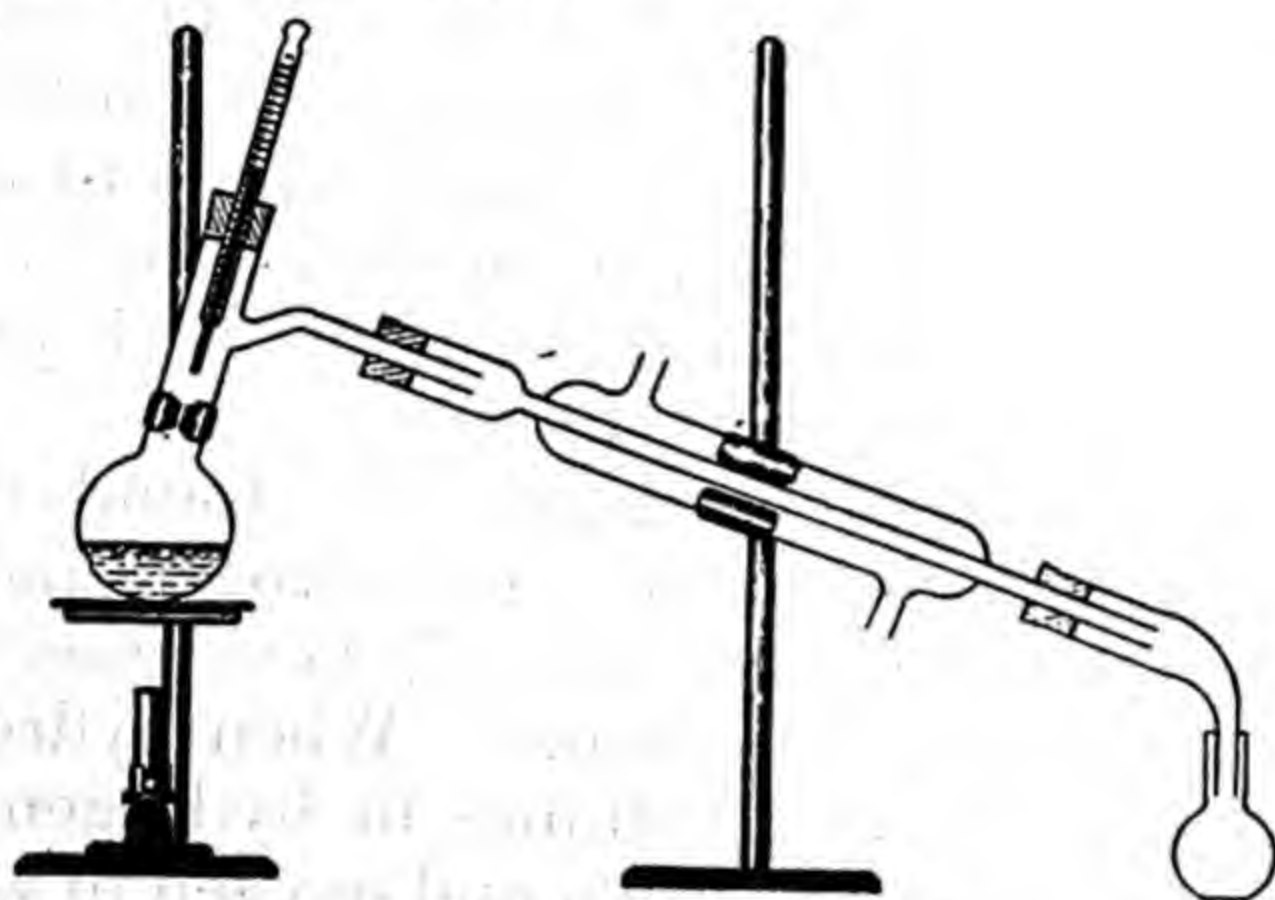


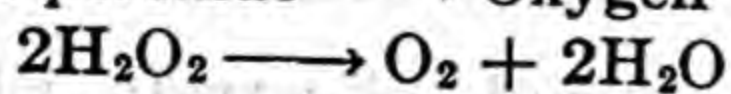
Fig. 51. Distillation of water.

Pure water is required for many laboratory processes, for the manufacture of ice, for use in storage batteries, and for many other purposes. Ships that make long voyages are equipped with distilling apparatus (stills) to prepare drinking water from sea water.

Hydrogen Peroxide

Another compound formed by the combination of hydrogen and oxygen atoms is called *hydrogen peroxide*. The molecule of this substance contains two atoms of hydrogen united with two atoms of oxygen. Pure hydrogen peroxide decomposes explosively, giving off oxygen and leaving water:

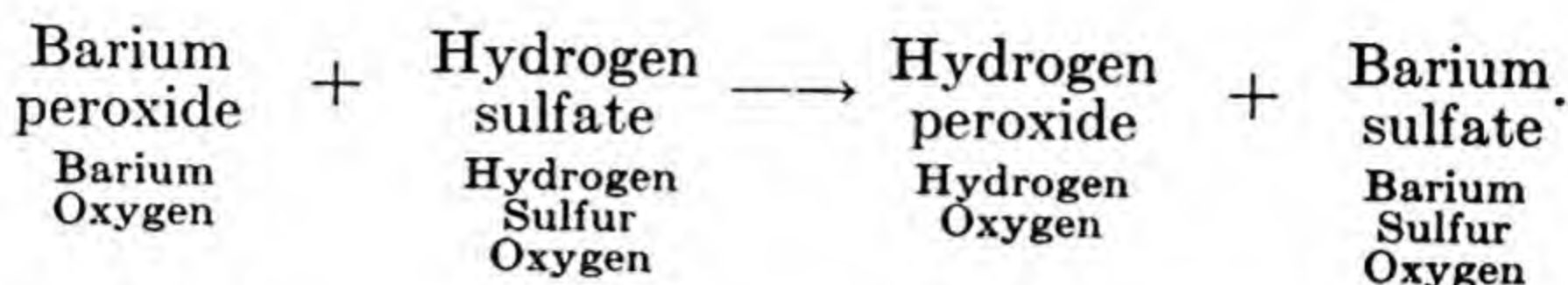
Hydrogen peroxide \longrightarrow Oxygen + Water.



A dilute solution (3 per cent) of hydrogen peroxide in water is fairly stable; but the decomposition into oxygen and water takes place quite rapidly in a bright light or when the solution is heated. For this reason, hydrogen peroxide is kept in brown-colored bottles

and in a cool place. The decomposition is retarded also by adding a small amount of acetanilide to the solution.

Preparation of hydrogen peroxide. Pure hydrogen peroxide is difficult if not dangerous to prepare, but a 3 per cent solution is made readily by the action of dilute sulfuric acid on barium peroxide:



Uses. Hydrogen peroxide decomposes rapidly in the presence of blood, and is often used to wash wounds. The rapid evolution of oxygen tends to release dirt particles and other impurities. Hydrogen peroxide is used as a bleaching agent to remove colors from such substances as silk, wool, feathers, and hair. Oxygen atoms released from the compound combine with pigments, converting them into colorless compounds.

The law of multiple proportions. We found that water is made by the union of two volumes of hydrogen and one volume of oxygen. When water is decomposed these gases are liberated in the ratio of two to one by volume. When hydrogen peroxide is decomposed it yields equal volumes of hydrogen and oxygen. The ratio of the weights of hydrogen and oxygen in water is 1 to 8. The ratio in hydrogen peroxide is 1 to 16. We have two compounds made of the same two elements, and we find that the weight of the oxygen combined with a certain weight of hydrogen in one is exactly twice the weight of the oxygen combined with the same weight of hydrogen in the other. The ratio of the weights of oxygen in the two compounds can be expressed by small whole numbers:

	Hydrogen by weight	Oxygen by weight	Ratio of the weights of oxygen
Hydrogen oxide (water).....	1	8	8 to 16 or 1 to 2
Hydrogen peroxide.....	1	16	

Water and hydrogen peroxide illustrate what is known as the *law of multiple proportions*.

When any two elements *A* and *B* combine to form more than one compound, the weights of *B* in the two or more compounds, if combined with a fixed weight of *A*, are in the ratio of small whole

numbers. We shall find further illustrations of this law when we study other elements which combine to form more than one compound.

Questions and Exercises

1. What is the ratio, by weight, of hydrogen to oxygen in water?
2. What fractional part of water is hydrogen?
3. What fractional part of water is oxygen?
4. What is the per cent of hydrogen and of oxygen in water?
5. What are the relative volumes of hydrogen and oxygen obtained from water by electrolysis?
6. Does water expand or contract when cooled from $20^{\circ}\text{C}.$ to $8^{\circ}\text{C}.$; from $8^{\circ}\text{C}.$ to $4^{\circ}\text{C}.$; from $4^{\circ}\text{C}.$ to $0^{\circ}\text{C}.$? How do most other liquids differ from water in this respect?
7. Which has the greater volume, 1 lb. of water at $0^{\circ}\text{C}.$ or 1 lb. of ice at $0^{\circ}\text{C}.$?
8. Wet towels when hung out to dry in winter often freeze; yet, ultimately, they dry even at a temperature below zero. Does ice have a vapor pressure? Explain the first statement.
9. Does the vapor escaping from water exert a pressure?
10. Why does wet laundry dry slowly on a rainy day even when not directly exposed to the rain?
11. Why does water become cooler as it evaporates?
12. How could you prove that water is formed in the gas flame of the kitchen range?
13. What products are formed when hydrogen gas is passed over hot copper oxide?
14. Which contains the greater amount of energy, water or an equal weight of ice? (Heat is a form of energy.)
15. A temperature somewhat below $0^{\circ}\text{C}.$ must be reached to damage growing plants. Farmers sometimes irrigate their fields when there is danger of frost. How does this practice protect the crop? (Note: 79 cal. of heat must escape from every gram of water that actually freezes.)
16. Your hand will be severely burned if held in steam from boiling water, but it can be held for a short time in an oven at the same temperature without injury. Explain. (Note: In one case, water vapor condenses on your hand, and in the other case water evaporates from your hand.)
17. Why does it take a long time to cook vegetables at high altitudes?
18. Why do vegetables cook quickly in a pressure cooker?

PART 5

Solutions

The natural waters which were described earlier are *solutions*. A sample of ocean water may be as clear as crystal, and look in all respects like pure water, but if we taste it we notice that it contains some substance other than water. It tastes much like ordinary table salt. It really contains table salt, but no matter how closely we examine it, even with a microscope, the particles of salt cannot be seen. Where are they? Ocean water is a solution, and in a solution the substance which is dissolved is uniformly distributed throughout the dissolving medium, and the particles of dissolved substance are either single molecules or still smaller units called ions. Single molecules and ions are too small to be seen even with the aid of a good microscope. The dissolved substance is called the *solute* and the dissolving medium is called the *solvent*. In the ocean, the solvent is water and the principal solute is salt.

By a simple experiment we can show that dissolved substances become uniformly distributed in the solvent. If a drop of red ink is dissolved in a beaker of water and the solution is stirred for a short time, every drop in the beaker acquires the same color as any other drop of the solution. If the molecules of ink were not separated but were in clumps, the color in some parts of the solution would be more intense than in others.

How do we know that the solute has not reacted with the solvent and formed a new chemical compound? We know that the two substances do not form a compound, for the relative amounts of the dissolved substance and the dissolving medium can be varied within wide limits. Such is not true of a compound. When water is formed from hydrogen and oxygen, we observe that the elements always combine in a definite proportion, no matter in what amounts they are mixed. If too much of either element is used, the excess is left over. When we analyze water we always find exactly the same ratio between the weights of the hydrogen and oxygen. Similarly for all compounds; they always have a definite composition by weight. Solutions do not. We may dissolve one gram of sugar in one liter of water or we may dissolve

10 or 50 g. of sugar in the same amount of water. We still have a solution of sugar in water. The law of definite proportions does not apply to a solution.

In at least one other way a solution differs from a compound. The components of a solution may be separated from each other by physical processes. Sugar may be recovered from a solution in water by evaporating the water. The constituents of a chemical compound cannot be separated in this way.

Solvents. The solvent may be a liquid other than water or it may be a solid or a gas. Since, however, water probably dissolves a greater number of substances than does any other agent known, aqueous solutions are the most common ones. Gasoline is a good solvent for fats whereas water is not, and for this reason gasoline is used in dry-cleaning processes.

Alcohol is often used as a solvent for substances which will not dissolve in water. Shellac dissolves in alcohol. Medicines dissolved in alcohol are called "tinctures." Tincture of iodine is such a solution.

Solutes. In the solutions so far mentioned the solute has been a solid. Solutes may also be liquids or gases. Alcohol and water form a solution and are soluble in all proportions. Liquids like alcohol and water are said to be *miscible* with each other. Air dissolved in water forms a solution, and ammonia gas is extremely soluble in water. Solids sometimes dissolve in solids. Glass is a solution of one solid in another. Air is commonly called a mixture of gases, but it is permissible to call it a solution of gases in gases.

Suspensions. Many substances form suspensions in water. Clay is often held in suspension in streams and rivers, and gives the water a turbid appearance. The particles may even be too small to be seen, but if the liquid is not perfectly transparent and clear, there are suspended particles present. The path of a beam of light in passing through such a suspension appears milky, but a beam of light passing through a true solution does not produce this effect. The particles of substance which are in suspension are not in the form of single molecules, but are small clumps or aggregates of many molecules.

Solubility. Usually only a definite amount of a solid solute can be held by a given quantity of liquid solvent at any given temperature, and when this limit is reached we have a *saturated solution*. If sugar is continually added to a cup of coffee, a point will be reached when no more sugar will dissolve. The remainder stays in the bottom of the cup in the solid form. The coffee has been saturated with sugar. At 25°C., 100 g. of water can dissolve at most 35.9 g. of sodium chloride or table salt. Such a solution is a

saturated solution of sodium chloride. The solubility of a substance varies with the temperature. Nearly all solid substances are more soluble in hot water than in cold water, but there are a few exceptions to this rule. Solutions of gases differ from those of most solids in that the solubility of any gas in a liquid or solid is dependent upon both the temperature and pressure. A gas becomes less soluble in a liquid or a solid as the temperature is raised, and more soluble as the pressure is increased. Gases are miscible with other gases in all proportions.

Some liquids are miscible in all proportions with certain other liquids. Alcohol and water illustrate this—a clear, homogeneous

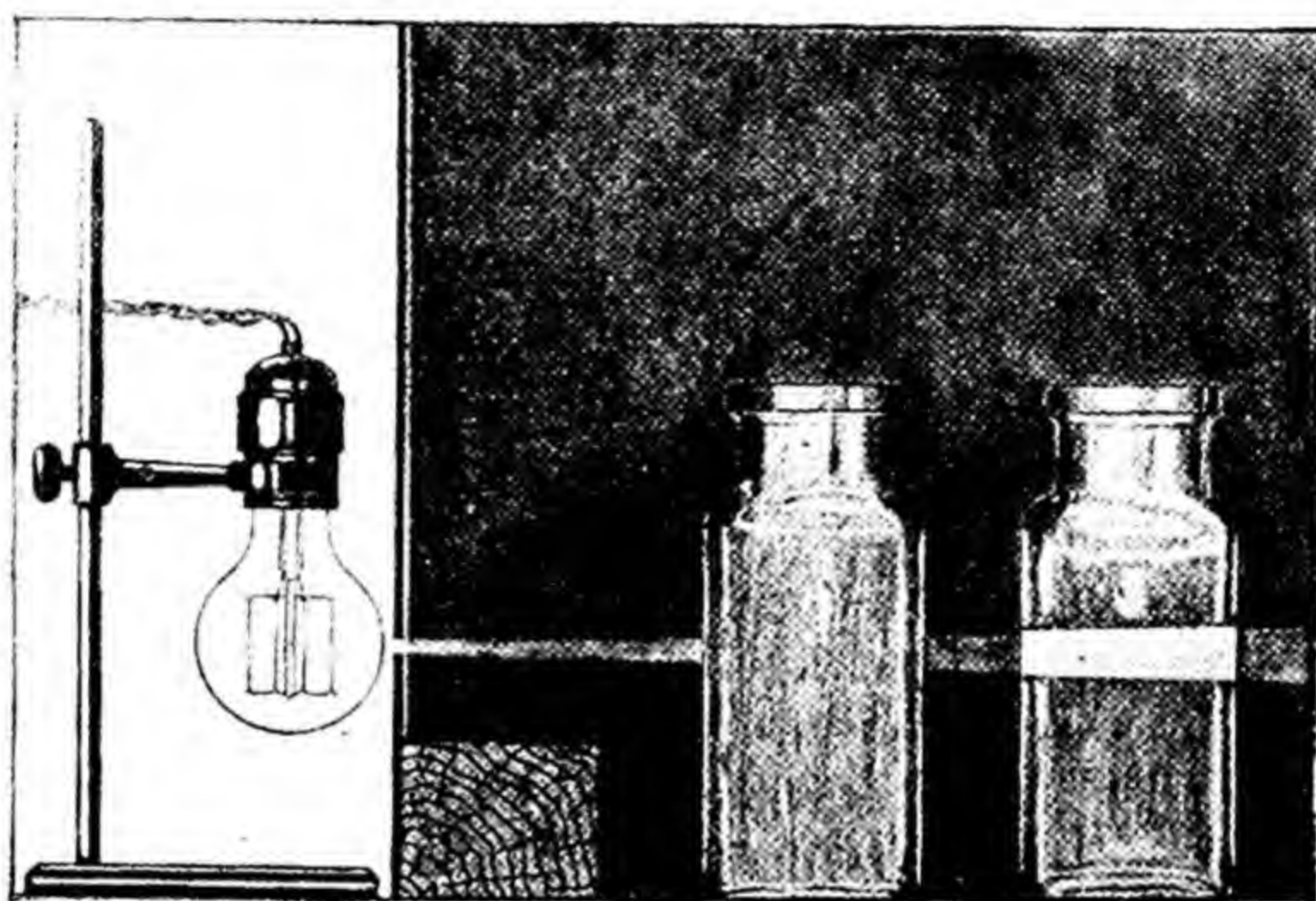


Fig. 52. Light makes a visible path through the jar containing fine particles in suspension. Its path cannot be seen in the jar filled with a true solution.

solution is obtained no matter what the relative amounts of alcohol and water may be. Ether and water, or chloroform and water, on the other hand, display limited solubilities when mixed in varying proportions. A saturation point is reached, as in the case of a solid solute in a liquid solvent. If more ether or chloroform is added than is necessary to saturate the water, the excess appears as a second liquid layer. Such liquids are said to be partially miscible. The water layer is saturated with ether or chloroform, and the ether or chloroform layer is saturated with water.

Some liquids are almost immiscible, such as water and mercury; but even in this case the mercury layer will be found to be saturated with water, and the water layer saturated with mercury.

Since the amount of solute required to saturate a solvent changes with the temperature, it is necessary to specify the temperature when we refer to the solubility of a substance. For example,

at $10^{\circ}\text{C}.$, 100 g. of water will dissolve 18 g. of a salt called potassium nitrate. At $60^{\circ}\text{C}.$, 100 g. of water will dissolve 110 g. of potassium nitrate. Suppose we heat 100 g. of water to $60^{\circ}\text{C}.$ and saturate it with potassium nitrate. The clear solution will contain 110 g. of the salt, and as long as we keep the temperature at $60^{\circ}\text{C}.$ or higher, no salt will settle out. If, however, we cool the solution to a tem-

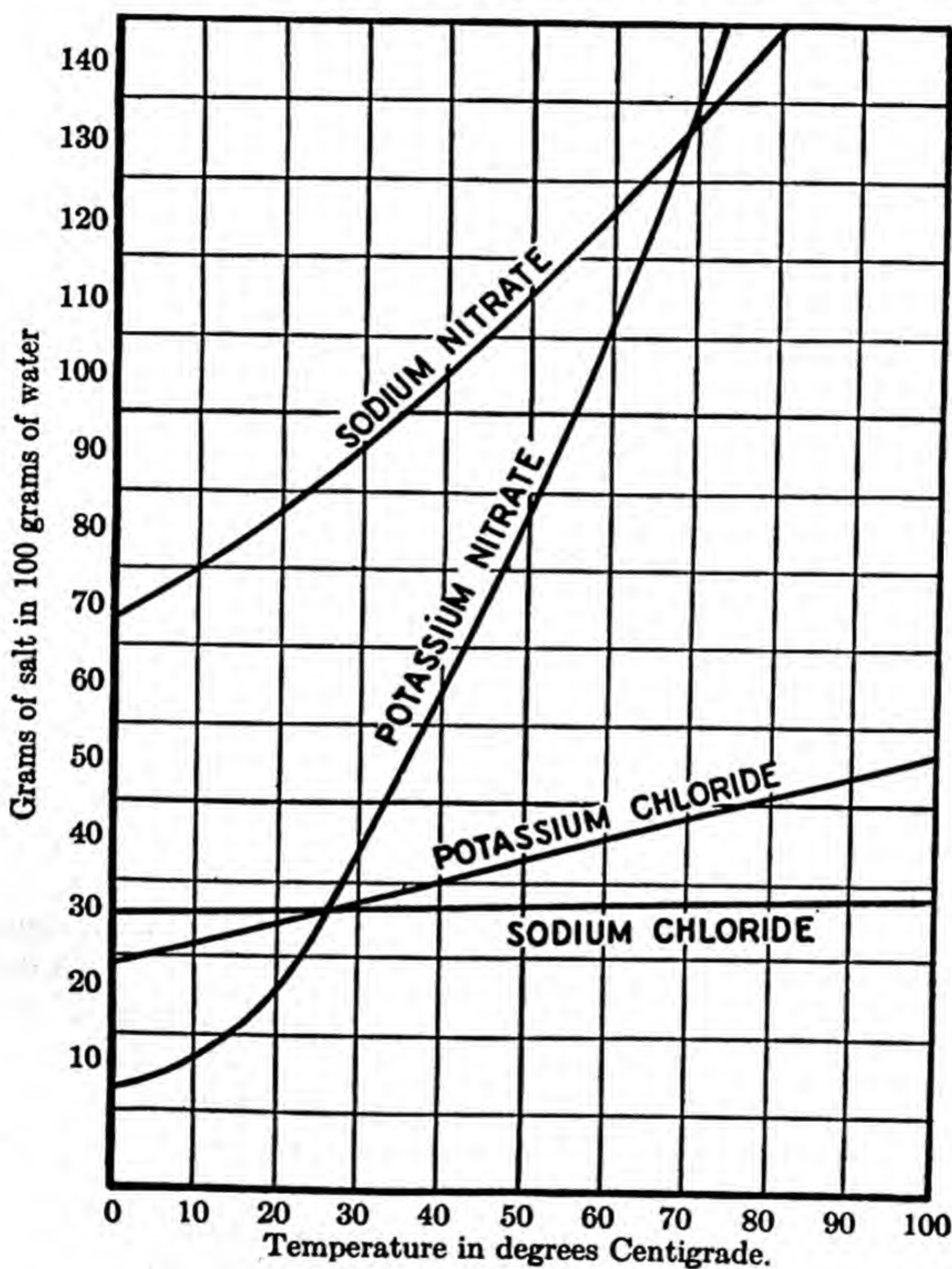


Fig. 53. Solubility curves.

perature below $60^{\circ}\text{C}.$, some of the potassium nitrate will crystallize and settle out of the solution (that is, it will precipitate). If the cooling is continued to $10^{\circ}\text{C}.$, there will be only 18 g. of the salt left in solution. There will be a solid residue of 92 g. of the salt on the bottom of the container. Solubilities of potassium nitrate, sodium chloride, potassium chloride, and sodium nitrate at various temperatures are shown graphically in Fig. 53. Notice that the

solubility of sodium chloride does not change very much when the solvent (water) is heated, while that of potassium nitrate changes rapidly.

The solubility of a solid is not changed appreciably by applying pressure to the liquid while it is in contact with the solid, but the solubility of a gas in a liquid depends upon the pressure applied. This principle is known as Henry's law. If the pressure on the gas is doubled, twice as much of the gas will dissolve. In the preparation of soda water, carbon dioxide is forced into the water under pressure and the solution is kept in sealed containers. Carbon dioxide accumulates in the neck of a soda-water bottle until the pressure of the liberated gas is sufficient to prevent further escape from the solution. When the stopper of a bottle is removed, the pressure is reduced and carbon dioxide bubbles out of the liquid.

It is a common practice to speak of strong solutions and weak solutions, but chemists prefer to use the terms *concentrated* and *dilute* instead of strong and weak. A *dilute solution* is one that contains very little dissolved substance. A *concentrated solution* is one that contains a large amount of dissolved matter.

Supersaturation. Some dissolved substances do not separate from the solvent promptly when a saturated solution is cooled. Sodium acetate, sodium sulfate, and the substance commonly called "hypo" (sodium thiosulfate), which photographers use in fixing negatives, form such solutions.

If warm water is saturated with a salt of this type, and the solution is then cooled, it may retain all the salt that dissolved in the water at the higher temperature. The cold water then contains more of the dissolved substance than an equal volume of cold water would dissolve if placed in contact with salt crystals. Such a solution is said to be *supersaturated*. When a small crystal of the salt is added to a supersaturated solution, some of the dissolved compound crystallizes, leaving in solution the same amount of the substance that would actually dissolve in the water at that temperature.

A beautiful demonstration of the phenomenon of supersaturation may be made as follows: dissolve 120 g. of sodium acetate in 100 cc. of boiling water. Place the flask containing the solution in a beaker or a pan containing a large volume of hot water. Cover the neck of the flask with a filter paper or a stopper to keep out dust particles and allow the solution to stand for two hours or more. The water surrounding the flask insures slow cooling. If no crystals form in the flask while cooling, drop into the solution a crystal of sodium acetate and observe the result. Crystallization may usually be started in a supersaturated solution by stirring

or shaking it or by scratching the walls of the container with any sharp tool.

A common example of the supersaturation of a gas in a liquid is found in ginger ale. The liquid contains the gas, carbon dioxide, dissolved under pressure. When the bottle is opened, the gas is not immediately evolved, but when the liquid is shaken or poured out of the bottle, the excess of carbon dioxide escapes. The escaping gas gives the ginger ale an appearance that we commonly describe as sparkling.

Hydrates. When water is evaporated from a solution of copper sulfate, deep blue crystals of the substance form. When these crystals are heated, water is given off and the blue crystals change to a white powder. If a little water is added to the white powder, a blue solution is formed, which on careful evaporation again yields blue crystals of copper sulfate.

Copper sulfate is an example of a class of substances called *hydrates*. Many substances crystallize from water solution with water molecules as part of the crystal. Not all crystalline substances contain water of hydration. Sodium chloride crystal, for example, contains no water of hydration. When a hydrate is heated to a suitable temperature, the water of hydration passes off, leaving an *anhydrous* residue. The word *anhydrous* (Greek) means *without water* or *deprived of water*.

Every hydrate contains a definite amount of water in a given weight of the crystalline substance. A hydrate, therefore, is a compound. In blue vitriol every molecule of copper sulfate is combined with five molecules of water. Washing soda, or sal soda, contains ten molecules of water combined with one molecule of sodium carbonate. Sodium sulfate, which occurs in nature as Glauber's salt, also contains ten molecules of water of hydration. Barium chloride, in the crystalline form, contains two molecules of water to the molecule. The water held in a hydrate is sometimes called *water of crystallization*, for the crystal form of the compound usually is destroyed when the water is driven off by heat. Hydrates have definite vapor pressures, just as liquids have, and the vapor pressures increase with the temperature, as do the vapor pressures of liquids.

Efflorescence. Some hydrates lose water at ordinary temperatures when they are exposed to the air. If the vapor pressure of a hydrate is greater than the pressure of water vapor in the surrounding air, water evaporates from the crystals when they are left in an open vessel. Washing soda, alum, and borax are hydrates of this kind. They form clear, firm crystals when allowed to crystallize from water, but become soft, noncrystalline powders as the water

of hydration passes off. In closed vessels (for instance, stoppered bottles) they remain crystalline, for escape of water is prevented, and the space above the crystals soon reaches the vapor pressure of the hydrate. Hydrates that lose water when exposed to the air at ordinary temperatures are said to *effloresce*.

Deliquescence. Some substances absorb water vapor from the air, and are said to be hygroscopic. Silk is somewhat hygroscopic. A silk garment always feels damp in rainy weather—it actually absorbs moisture from the atmosphere. There are many hygroscopic compounds that take up indefinite quantities of water and fail to form hydrates. True hydrates are crystalline,

and they follow the law of definite proportions. A hygroscopic substance which continues to absorb water from the air until it becomes wet (that is, covered with a liquid layer) is *deliquescent*. Calcium chloride and solid sodium hydroxide are compounds of this type.

Deliquescent substances find extensive use in removing the moisture from air. Substances are often dried in a desiccator (Fig. 54), which provides an atmosphere free from water vapor. Calcium chloride, a deliquescent compound, is placed in the bottom of the desiccator. The substance to be dried is placed in a dish above the drying

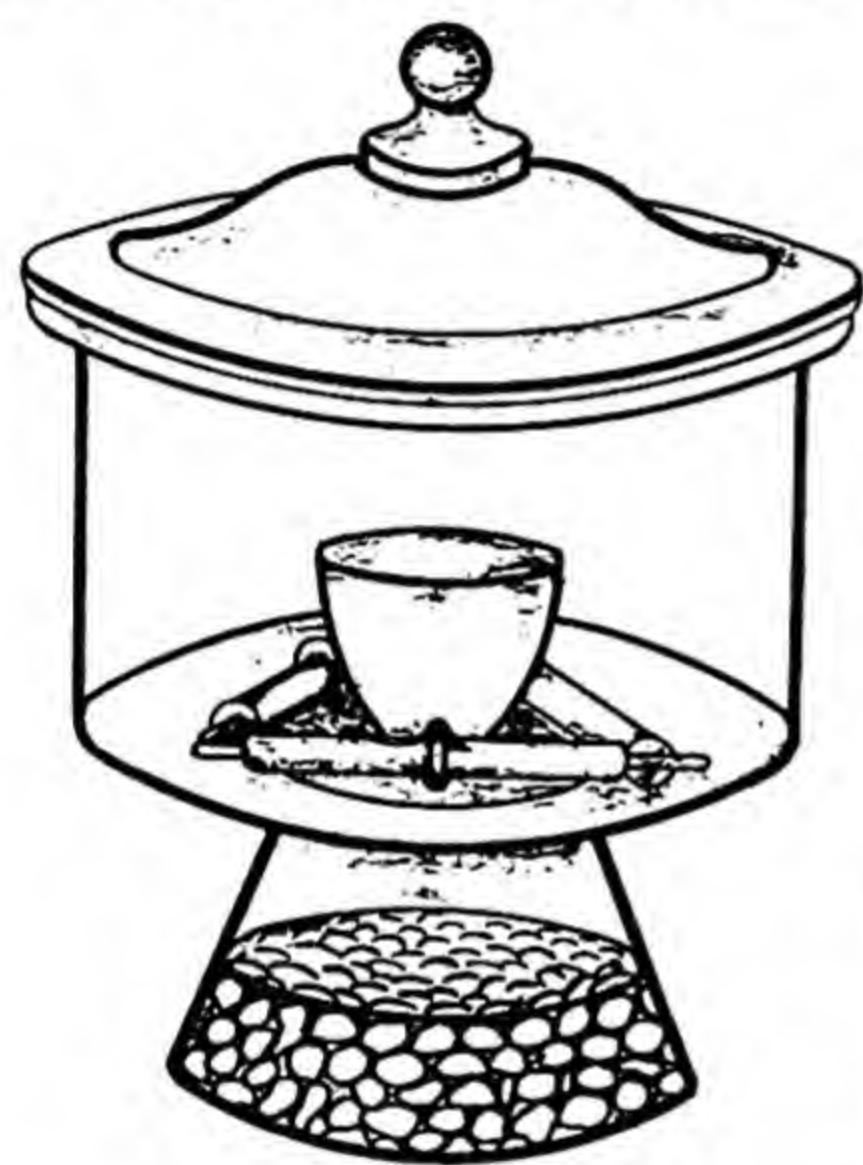


Fig. 54. A desiccator.

agent. Water evaporates from the moist sample and is absorbed by the calcium chloride.

Nonvolatile solutes and vapor pressure. We have learned that the space above a liquid in a closed container always contains a definite number of molecules in the gaseous state, at any given temperature. (See page 68.) We have learned also that these vapor molecules are in equilibrium with the liquid, that is, just as many return to the liquid state as escape from it during any period of time, so that the number of molecules in the vapor state is constant.

Suppose we dissolve in water a solute like sugar, which has no vapor pressure of its own; let us dissolve enough sugar to make one-tenth of the molecules sugar molecules, and nine-tenths of them water molecules. We find, by experiment, that the number of water molecules in the vapor state over the solution in a closed container, and hence its vapor pressure, is now nine-tenths of

what it originally was. The vapor pressure of the water molecules above a solution containing a nonvolatile solute is proportional to the fraction of water molecules in the solution. In Fig. 55 the dotted line shows the vapor pressure of water molecules over a solution in which nine-tenths of the molecules are water molecules.

The lowering of the vapor pressure is independent of the solute used, if the solute has no vapor pressure of its own, and if it remains in the molecular state when in solution. A solution of a protein shows the same lowering of the vapor pressure as one containing glycerine, provided that the same number of molecules of the solute are dissolved in each case, although the protein molecule is probably 400 times as heavy as the glycerine molecule.

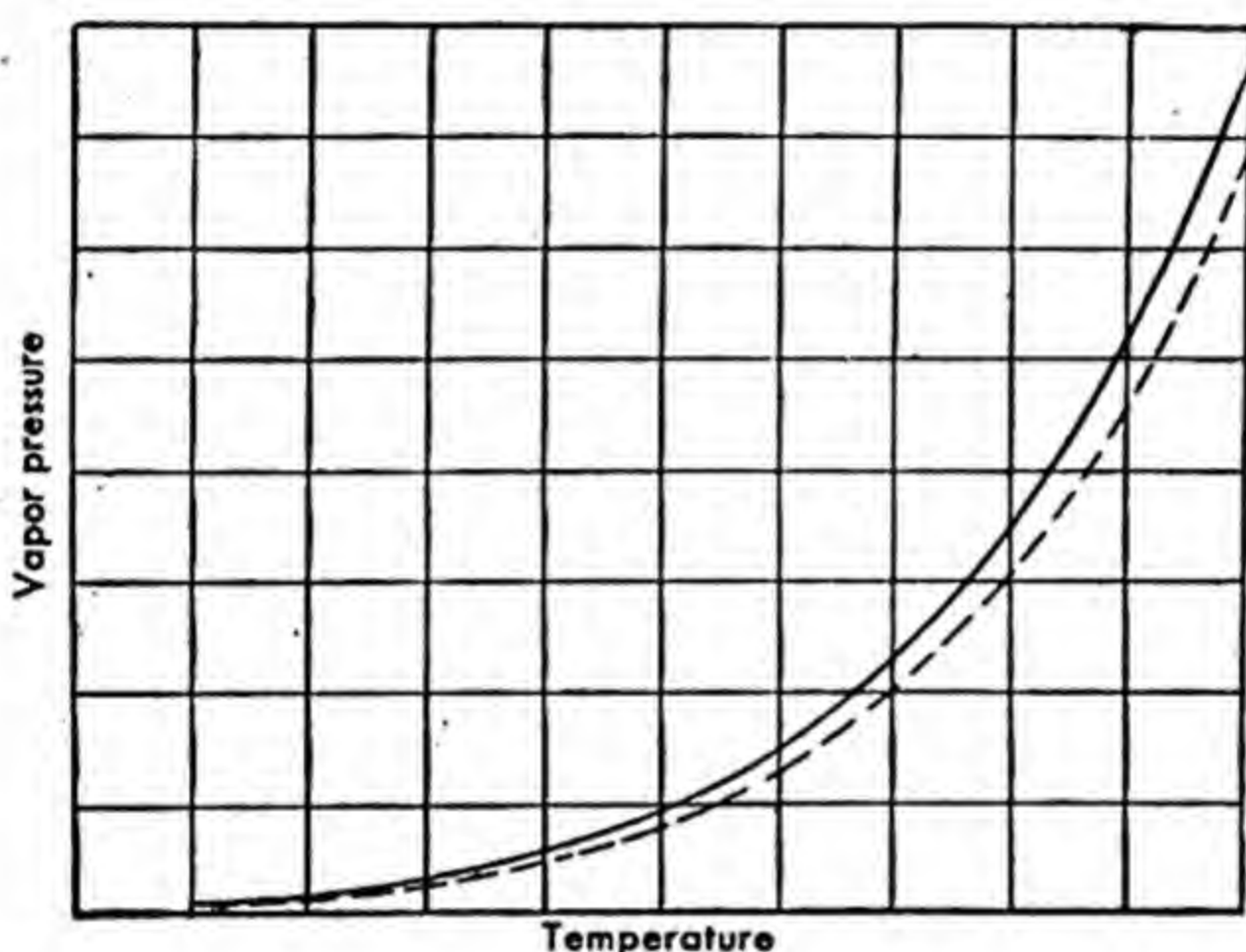


Fig. 55. The vapor pressure of pure water (solid line) and the vapor pressure of a solution in which nine tenths of the molecules are water molecules (dotted line).

In other words, it is the number of solute molecules, not their size or weight, which affects the vapor pressure of the solvent. Hence, *the vapor pressure of a solution containing a nonvolatile solute is proportional to the fraction of the total number of molecules that are solvent molecules in the solution.* This behavior is an illustration of Raoult's law. In general, Raoult's law states that the vapor pressure of the solvent escaping from a solution is proportional to the fraction obtained when we divide the number of solvent molecules by the total number of molecules in the solution. This rule does not apply if the dissolved substance is volatile, or if the dissolved substance is present in high concentration, and we shall find later that three classes of substances—acids, bases, and salts—have a comparatively greater effect on the vapor pressure of a solvent than do substances like sugar, glycerine, and proteins.

Elevation of the boiling point. The boiling point of a liquid has been defined as the temperature at which its vapor pressure is equal to one atmosphere. Similarly, the boiling point of a solution is the temperature at which its vapor pressure is equal to one atmosphere. Since the vapor pressure of the solvent in a solution is lower than that of the same liquid when pure at any temperature, it is evident that the boiling point of a solution containing a nonvolatile solute is always higher than that of the pure solvent. Figure 56 illustrates this fact.

If we place a thermometer in a boiling solution of sugar, we find that the temperature is above $100^{\circ}\text{C}.$, the boiling point of the pure solvent, water. We shall also find that the temperature continues to rise as water boils off from the solution. In other words, the more concentrated the sugar solution becomes, the higher is its boiling point. The boiling point of a solution made by dissolving the molecular weight in grams of a nonvolatile solute in 1000 g. of water is $100.518^{\circ}\text{C}.$ In other words, the *elevation* of the boiling point is 0.518° . A solution which contains twice the gram molecular weight of solute per 1000 g. of water shows an elevation of $2 \times 0.518^{\circ}$, and boils at $101.036^{\circ}\text{C}.$ The more concentrated we make the solution the higher the elevation of the boiling point will be, but this exact value (0.518° per mole of solute in 1000 g. of water) applies to dilute solutions only.

Lowering of the freezing point. Many of us have observed that if the temperature drops during a winter night, a fresh-water lake freezes when the temperature is only a fraction of a degree below $0^{\circ}\text{C}.$, but a salt-water lake does not freeze until the temperature has dropped to several degrees below zero. A solution always has a lower freezing point than that of the pure solvent. When the molecular weight in grams of a substance like sugar is dissolved in 1000 g. of water, the freezing point is $-1.86^{\circ}\text{C}.$ Twice as much sugar in 1000 g. of water lowers the freezing point $2 \times 1.86^{\circ}$, and such a solution freezes at $-3.72^{\circ}\text{C}.$ A substance like salt has even a greater effect on the lowering of the freezing point of a solution than sugar has (see page 216).

We use this principle when we make ice cream. Milk and cream freeze below $0^{\circ}\text{C}.$, and would not solidify if merely surrounded by ice or snow alone under atmospheric pressure. Salt is added to the ice, causing some of the ice to melt and form a brine. Every gram of ice which melts absorbs 79 cal. of heat from the brine, lowering its temperature, eventually, to the freezing point of the brine. At this low temperature the cream freezes. Artificial ice is manufactured by a similar process.

In winter we put antifreeze compounds in the radiators of our automobiles to prevent freezing. The solutes are added in sufficient amounts to make the freezing point of the solution considerably below the temperature which the outside air is likely to attain.

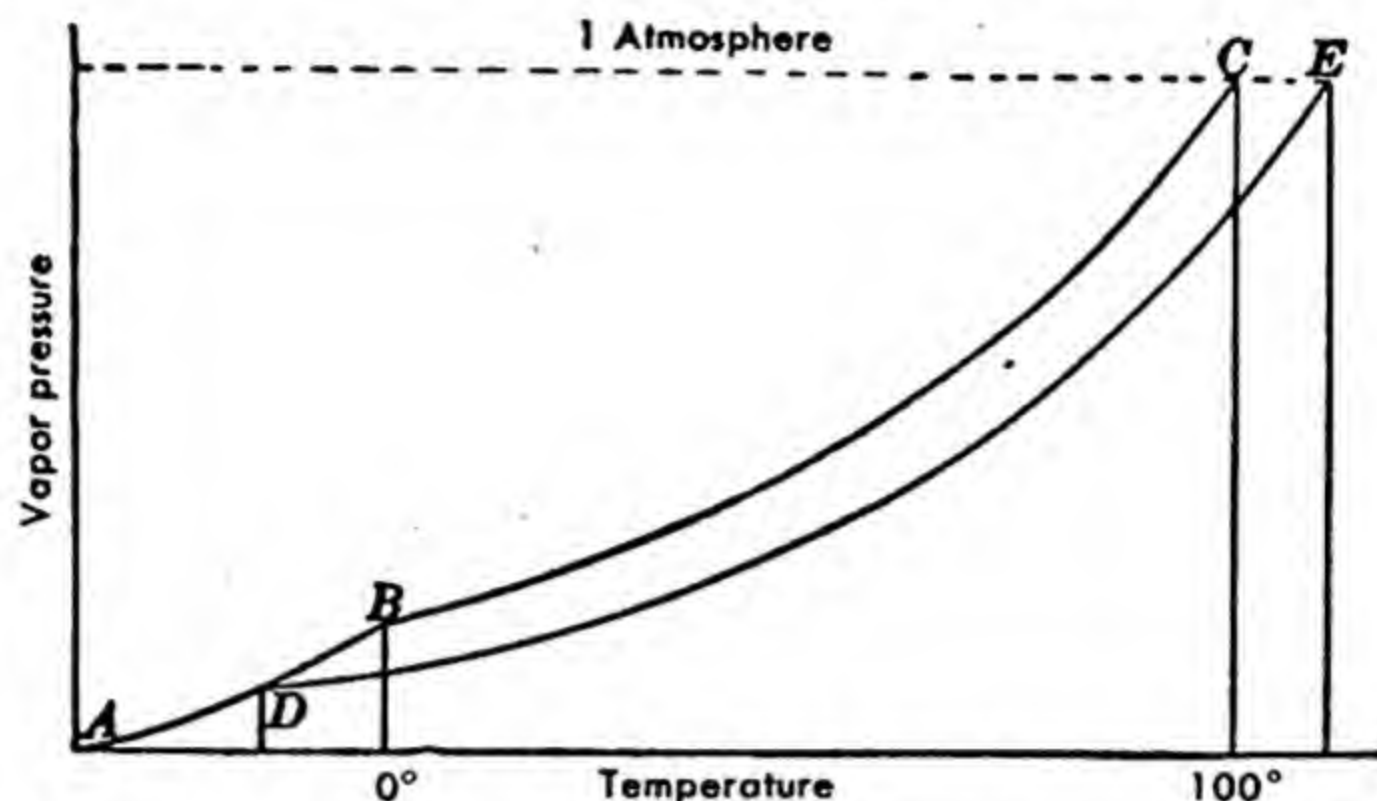


Fig. 56. AB = Vapor pressure of ice. BC = Vapor pressure of water. DE = Vapor pressure of a solution. The solution freezes below 0° and boils above 100° .

siderably below the temperature which the outside air is likely to attain.

Osmosis. This phenomenon may be illustrated by means of a simple apparatus. A piece of cellophane or a strip of parchment paper is tied tightly over the bell of a thistle tube. Cellophane or paper parchment allows small molecules, like those of water, to pass through; but large molecules like those of sugars or proteins cannot get through the membrane. The latter, therefore, is called a *semipermeable* membrane. If the thistle tube is filled with water and inverted in a beaker of water, as illustrated in Fig. 57, nothing seems to happen. Molecules of water are doubtless moving through the membrane in both directions, but they move both ways at the same rate so that the level of water in the thistle tube does not change. If, however, some of the molecules of water in the thistle tube are replaced by sugar molecules, which are too large to pass through the membrane, a change in the level of the liquid in the thistle tube is soon observed. The solution gradually rises in the tube. Water molecules on the outside of the membrane are free to move as independently as they were at the beginning of the experiment, and they pass through the membrane at the same

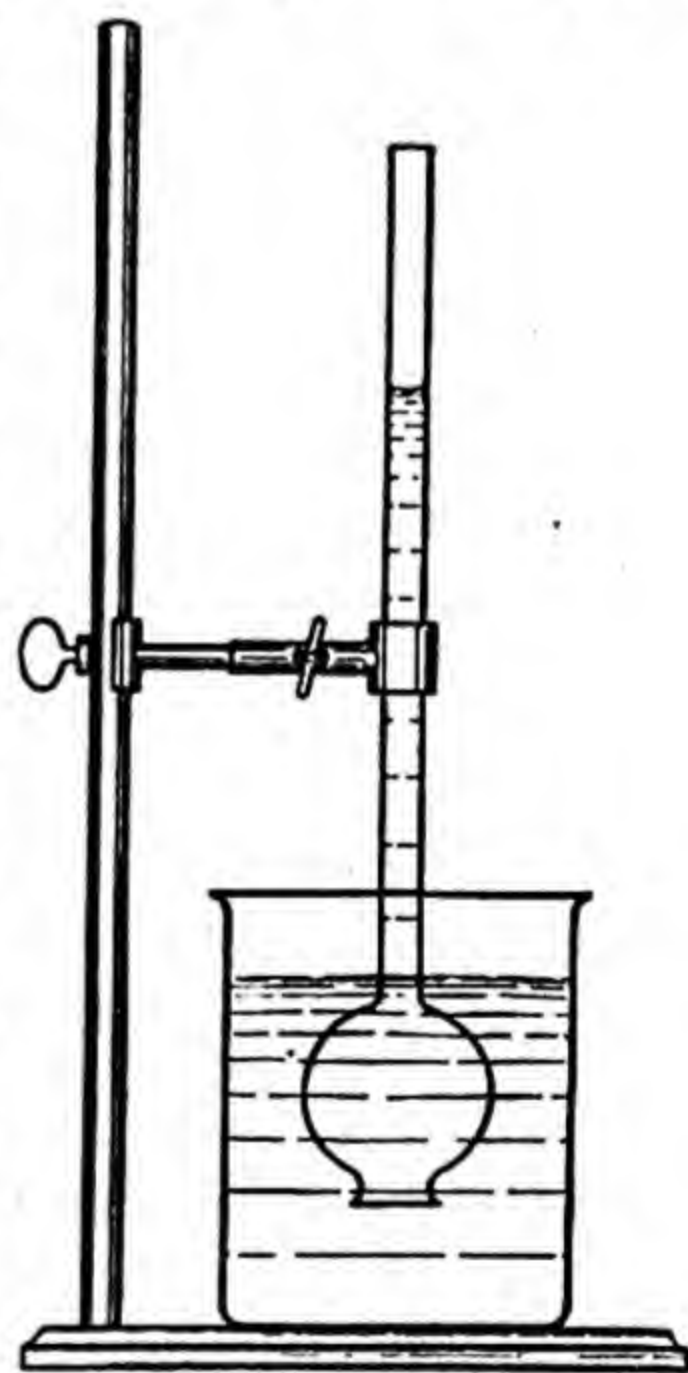


Fig. 57. Osmosis.

rate as before. The concentration of water molecules inside the thistle tube has been reduced, so that they pass outward at a slower rate. Hence the solution in the thistle tube becomes gradually diluted, with a corresponding increase in volume. This passage of molecules from the pure solvent through a semipermeable membrane at a faster rate than they pass from the solution into the pure solvent is called *osmosis*. Solvent molecules will pass, in the same manner, from a dilute solution to a more concentrated solution.

As the column of liquid grows in height, its weight presses down on the solution in the thistle tube, tending to force molecules of solvent out through the membrane at a faster rate. Eventually the weight of the column of solution exerts enough pressure on the solution to force solvent molecules out at the same rate at which they are entering. This pressure is called the *osmotic pressure* of the solution.

Questions and Exercises

1. How does a solution differ from a compound? How does it differ from a mixture? How does a compound differ from a mixture?
2. Name three common solvents.
3. What is (a) a solvent, (b) a solute, (c) a saturated solution, (d) a concentrated solution, (e) a dilute solution, (f) an unsaturated solution, (g) a supersaturated solution?
4. What single test could be made to determine whether a solution of sodium acetate is unsaturated, saturated, or supersaturated?
5. Give an example of a solution of (a) a gas in a liquid, (b) a liquid in a liquid, (c) a solid in a liquid, (d) a solid in a solid.
6. How does the solubility of a solid in a liquid vary with the temperature of the solvent? Does the solubility of a gas follow the same rule?
7. Is your drinking water pure, or does it contain dissolved substances? How can you settle this question experimentally?
8. Distinguish between efflorescence and deliquescence.
9. Make a list of the new words you have learned in this chapter.
10. In arid regions, blue vitriol becomes coated with a white powder. Explain.
11. Seed wheat is treated with a solution of blue vitriol to kill undesirable fungi. If you were buying blue vitriol for this purpose at a fixed price per pound, would you object to receiving the white powder instead of clear blue crystals?
12. At what temperature are sodium chloride and potassium nitrate equally soluble? (See the solubility curves, page 81.)
13. Give two reasons for believing that ocean water is a solution and not a pure compound.
14. Classify the following as solutions or compounds: (a) air, (b) water, (c) brass, (d) milk, (e) sugar, (f) salt.

PART 6

Kinetic Theory

Many chemical reactions involve gases. We have studied the preparation and properties of hydrogen and oxygen, and we are familiar with the properties of the atmosphere, which is a mixture of gases. Some of the elements which we shall study in the future form gaseous compounds. Since all gases act alike in many ways, it is important to know something about the behavior of this class of substances.

Gas molecules, under ordinary conditions, are separated from each other by spaces that are immense in comparison with the size of the molecules themselves. Our study of hydrogen showed us that the molecules of a gas are in motion. We found that hydrogen, the lightest known gas, becomes mixed with air when an open bottle of hydrogen is inverted *over* a bottle of air. If the molecules of hydrogen were not in motion, darting rapidly throughout the container, they would remain in the upper bottle and would not become mixed with the much heavier oxygen and nitrogen molecules in the lower bottle. Some molecules of oxygen and nitrogen also travel up into the bottle of hydrogen, showing that these molecules also are in motion.

The molecules of a gas may be pushed more closely together by increasing the pressure on the gas. Everything in the world tends to occupy a smaller volume when pressure is applied. We have all witnessed the closing of an overloaded suitcase by the convenient method of sitting on the cover. The pressure forces the contents of the suitcase more closely together so that they occupy a smaller volume.

The molecules of a solid are already close together, and a limit is soon reached beyond which we cannot further compress a solid by ordinary pressures. Gases are susceptible of large changes in volume because of the great spaces between the molecules.

Boyle's law. All of us who have pumped air into a bicycle tire or an automobile tire know that a great many more molecules of air can be forced into a given space than are ordinarily contained in

that space. This packing is accomplished by putting a greater pressure on the air. If the pressure is removed, the molecules spread out again and occupy a greater volume.

The effect of pressure on a gas can easily be demonstrated by means of an ordinary hand pump. First let us insert a tight plug in the outlet of the pump so that molecules cannot escape. If we now press down on the handle of the pump, the piston exerts a greater pressure on the gas contained in the cylinder. The molecules of gas are pushed more closely together, and hence occupy a smaller volume. As soon as the pressure on the handle is released, the piston springs back to its original position.

The exact relationship between the pressure on a gas and its volume was explained by the great scientist Robert Boyle. In

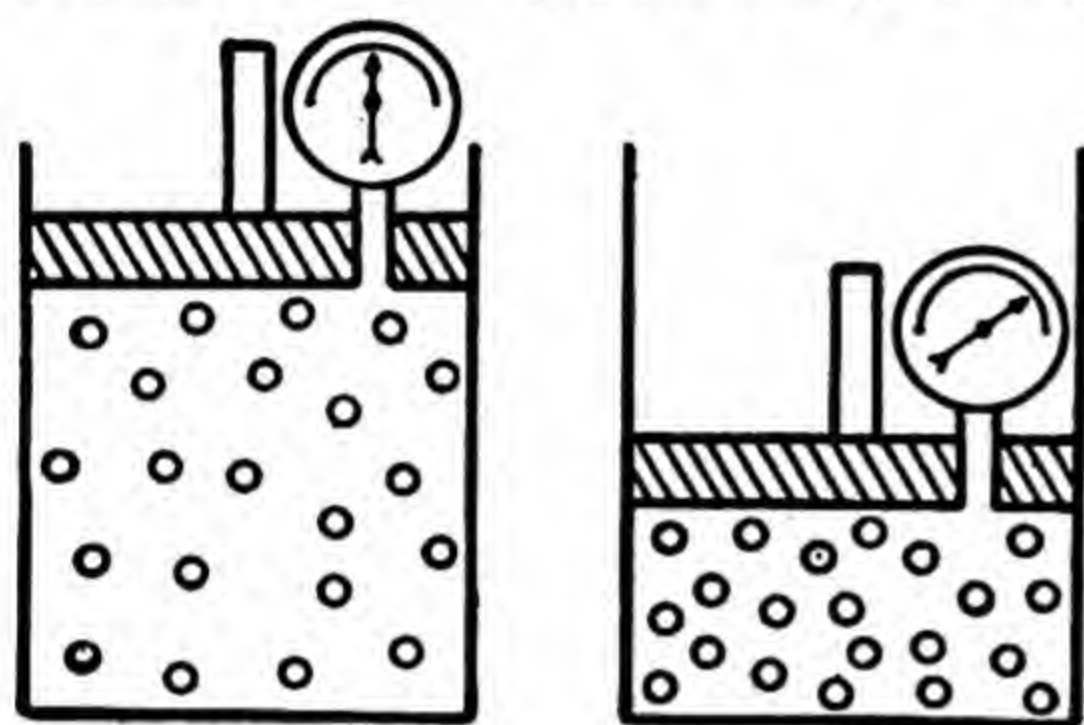


Fig. 58. Diagram showing the compression of a gas.

1662 he discovered that when the pressure on a gas is doubled, the gas occupies half of its original volume; under three times as great a pressure, its volume becomes one-third of the original volume; under a pressure one-half as great as the original pressure, the gas occupies twice the volume which it originally occupied; and so on. Boyle's law is usually stated as follows: *The volume of a*

gas varies inversely as the pressure, if the temperature remains constant.

In Unit II (page 33) we learned that the barometer is used for measuring the pressure of the atmosphere, which is a mixture of gases. The pressure of any gas can be measured by the height at which it holds a column of mercury. The average pressure of the air at sea level is called *one atmosphere*.

Let us suppose that we have 1 liter (1000 cc.) of oxygen under a pressure of 1 atmosphere in a cylinder provided with a gastight piston. If now we increase the pressure on the piston until we have the equivalent of 2 atmospheres compressing the gas, we find that the gas occupies only 500 cc. Doubling the pressure on the gas has halved the volume. If the pressure on the piston is changed to 3 atmospheres, the gas will occupy 333 cc. If the pressure on the piston is reduced to $\frac{1}{2}$ atmosphere, the molecules of gas spread apart and occupy 2 liters.

Gas-law problems in which the pressure is expressed in centimeters or millimeters are solved in exactly the same way as when pressure is expressed in atmospheres. Some examples will make this clear.

EXAMPLE 1. Under 750 mm. pressure, a gas has a volume of 425 cc. What volume will the gas occupy if the pressure is changed to 335.5 mm.? The pressure is reduced from 750 mm. to 335.5 mm., and the volume will increase. We therefore multiply the volume by the ratio of the pressures, placing the larger one in the numerator, since this will give us a larger answer:

$$425 \times \frac{750}{335.5} = 950.1 \text{ cc.}$$

The volume of the gas becomes 950.1 cc. under a pressure of 335.5 mm. of mercury.

EXAMPLE 2. Two bulbs (A and B, Figure 59) are connected with each other by a stopcock. Vessel A has a capacity of 425 cc. and is filled with air under a pressure of 75 cm. of mercury. Vessel B, which has

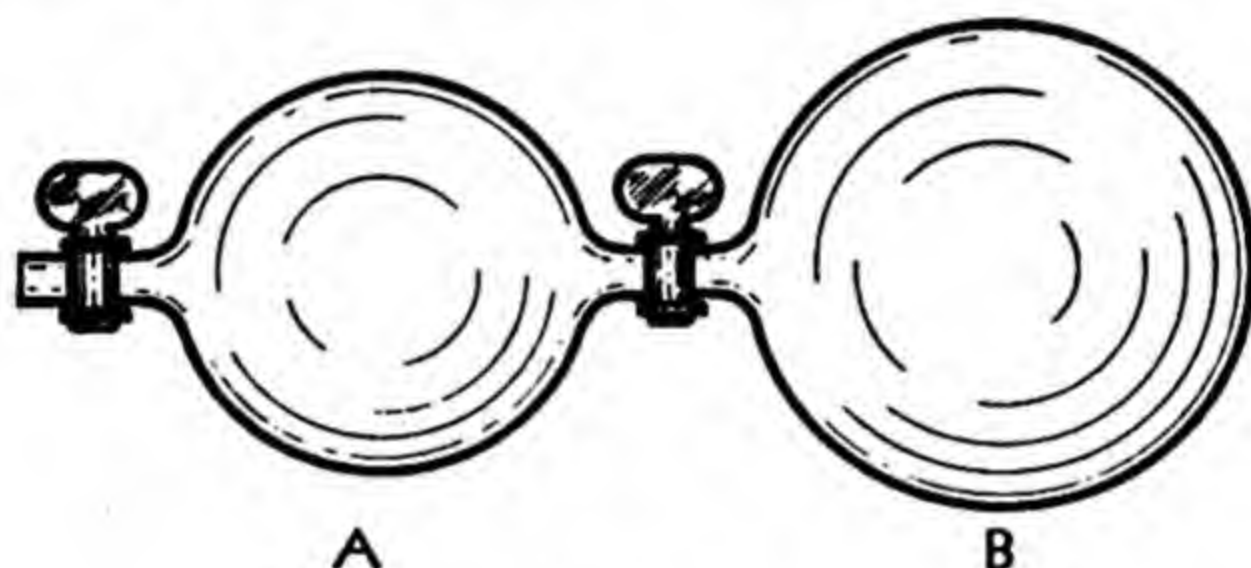


Fig. 59.

a capacity of 525 cc., is evacuated. If we open the stopcock between the two bulbs and allow the gas to fill both vessels, what will be the new pressure of the gas? The pressure will now be the same in the two bulbs. The new volume will be the sum of the two individual volumes of the bulbs, $425 + 525$, or 950 cc. We have expanded the gas from 425 to 950 cc. and by this expansion we have lowered the pressure. The new volume is $\frac{950}{425}$ times as great as the original volume. The new pressure, therefore, will be $\frac{425}{950}$ times as great as the original pressure. (The pressure is *inversely* proportional to the volume.) Solving this proportion, we have

$$75 \times \frac{425}{950} = 33.55 \text{ cm. or } 335.5$$

Charles's law and absolute zero. When any substance is heated, the molecules acquire energy and tend to separate from each other; that is, they get farther apart. This separation causes the substance as a whole to have a larger volume. When a gas is heated, it expands more rapidly than does either a solid or a liquid; when it is cooled, it contracts. Charles, a French scientist,

found the amount of this expansion and contraction. He discovered that, if he started with a given volume of air at a temperature of $0^{\circ}\text{C}.$ and heated it to $1^{\circ}\text{C}.$, the amount of its expansion was $\frac{1}{273}$ of its original volume. If he heated the air to $10^{\circ}\text{C}.$, its volume increased $\frac{10}{273}$ of its original volume; at $100^{\circ}\text{C}.$, the expansion was $\frac{100}{273}$; and at $273^{\circ}\text{C}.$, the increase in volume was $\frac{273}{273}$ of the volume the gas had at $0^{\circ}\text{C}.$ In other words, heating the gas $273^{\circ}\text{C}.$ doubled its volume.

Charles found also that when the gas was cooled from $0^{\circ}\text{C}.$ to $-1^{\circ}\text{C}.$, the contraction in volume was $\frac{1}{273}$ of its volume at $0^{\circ}\text{C}.$; when it was cooled to $-100^{\circ}\text{C}.$, the contraction was $\frac{100}{273}$ of its volume at $0^{\circ}\text{C}.$ This rule of expansion and contraction is true not only for air but for all gases.

What would happen to a gas if it were cooled from $0^{\circ}\text{C}.$ to $-273^{\circ}\text{C}.$? It would contract $\frac{273}{273}$ of its volume; in other words, it would have *no volume* at $-273^{\circ}\text{C}.$ Scientists believe this temperature, $-273^{\circ}\text{C}.$, is the lowest temperature that can ever be reached, and it is called *absolute zero*. Many attempts have been made in the laboratory to attain this low temperature. Actually a temperature within 0.2° of the absolute zero has been reached.

A temperature scale in which $-273^{\circ}\text{C}.$ is made the zero point has been devised. Temperatures measured on this scale are *Absolute temperatures*. The divisions are of the same size as those on the Centigrade scale. A comparison of the Absolute and Centigrade scales is shown in Fig. 60. It is seen that any tempera-

ture reading on the absolute scale may be obtained by adding 273 to the reading on the Centigrade thermometer. Thus $10^{\circ}\text{C}. = 10 + 273 = 283^{\circ}\text{A}.$ (absolute), and $50^{\circ}\text{C}. = 50 + 273 = 323^{\circ}\text{A}.$

According to Charles's law, a gas at absolute zero has zero volume, but all gases become liquids before that temperature is reached, and this law of contraction does not apply to liquids. At $273^{\circ}\text{A}.$ ($0^{\circ}\text{C}.$) let us say that a gas has a volume V . If the Absolute temperature is tripled (raised to $3 \times 273 = 819^{\circ}\text{A}.$), the gas will occupy a volume equal to $3V$. We must bear in mind that doubling the Centigrade temperature of a gas does not double the volume. If a gas is heated from $10^{\circ}\text{C}.$ to $20^{\circ}\text{C}.$, its volume is *not* doubled. The new volume is only $\frac{293}{283}$ of the original volume.

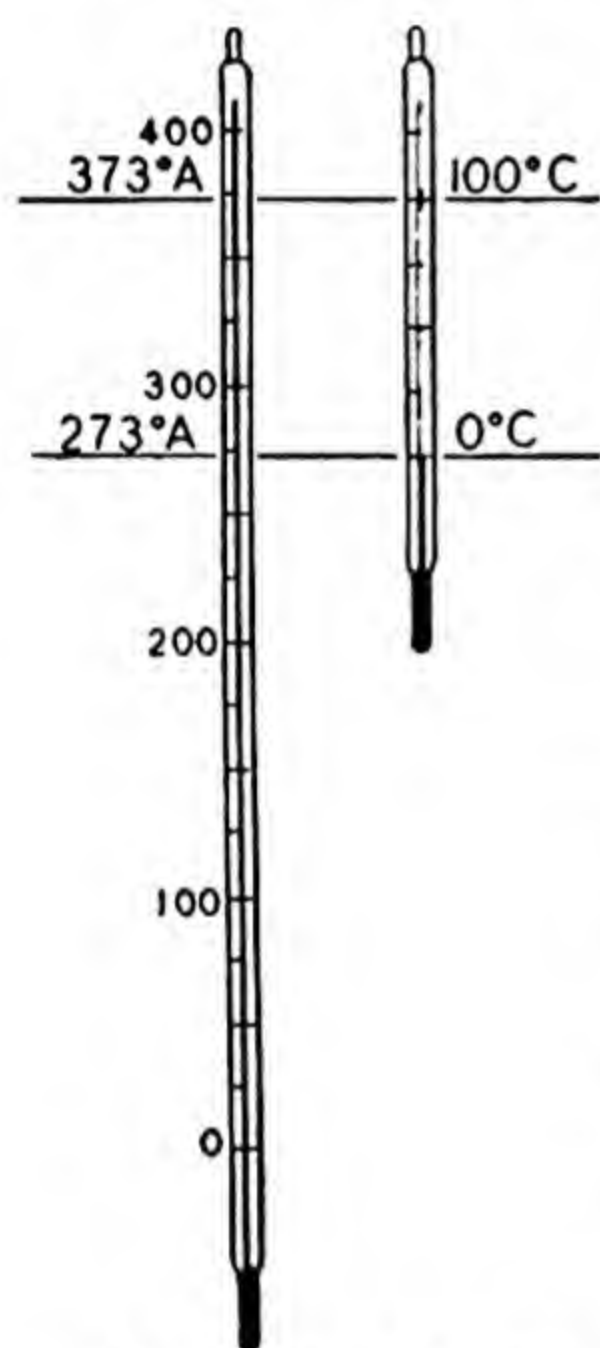


Fig. 60. A comparison of the Centigrade and absolute thermometers.

We may now state the *law of Charles* more definitely: *The volume of gas at constant pressure varies directly as the absolute temperature.*

An example will make clear the use of this law. Let us suppose that we have 1000 cc. of hydrogen at a temperature of 10°C. , or 283°A. What volume will it occupy at 60°C. or 333°A. ?

Since a gas expands when heated, we know that the volume of the hydrogen is greater at 333°A. than it is at 283°A. We therefore multiply the original volume by $\frac{333}{283}$:

$$1000 \times \frac{333}{283} = 1176.7 \text{ cc.}$$

Likewise, if a gas is cooled, its volume decreases proportionately. What volume will our hydrogen, which occupied 1000 cc. at 10°C. (283°A.) have at -50°C. ($-50 + 273 = 223^{\circ}\text{A.}$)? We know that when a gas is cooled, it has a smaller volume. Therefore we multiply the original volume by a fraction having the *smaller* temperature in the numerator.

$$1000 \times \frac{223}{283} = 787.9 \text{ cc.}$$

The gas will occupy 787.9 cc. at -50°C.

Problems involving a change in both temperature and pressure. The laws of Charles and Boyle may be applied simultaneously in the calculation of the change in the *volume, pressure, or temperature* of a gas when any two of these are changed.

PROBLEM 1. The volume of a gas measured at 55°C. and 760 mm. is 620 cc. Find its volume after the temperature has been changed to -7°C. and the pressure to 600 mm.

The temperature change (cooling) tends to decrease the volume. On the absolute scale the change is from 328° to 266° . The temperature effect would cause the gas to shrink to $\frac{266}{328}$ of its original volume. The pressure change is from 760 to 600 mm. This is a reduction in pressure which permits the gas to expand. The effect of the pressure change alone would be to increase the volume to $\frac{760}{600}$ of its original value. To obtain the result due to both of these changes we must multiply the original volume by both of these fractions:

$$620 \times \frac{266}{328} \times \frac{760}{600} = 637 \text{ cc.}$$

A convenient algebraic form of the combined gas laws is:

$$\frac{PV}{T} = \frac{P'V'}{T'}$$

In this equation, P , V , and T stand for the pressure, volume, and absolute temperature of the gas in its original condition, and P' , V' , and T' stand for the pressure, volume, and absolute temperature of the gas in its final state. Let us make use of this equation in the solution of a problem.

PROBLEM 2. A quantity of gas occupies 350 cc. at 40°C. and 550 mm. Find the pressure required to make it occupy 400 cc. at 27°C.

<i>Original conditions</i>	<i>Final conditions</i>
$P = 550$	$P' = \text{unknown}$
$V = 350$	$V' = 400$
$T = 313$	$T' = 300$

Using the formula, we have

$$\frac{PV}{T} = \frac{P'V'}{T'} \quad \text{or} \quad \frac{550 \times 350}{313} = \frac{P' \times 400}{300}.$$

Clearing the fractions, we obtain

$$P' \times 400 \times 313 = 550 \times 350 \times 300.$$

$$P' = \frac{550 \times 350 \times 300}{400 \times 313} = 461.3 \text{ mm.}$$

The problem may be solved as well without resorting to the formula. We may think of the conditions in this way: The new volume (400 cc.) is greater than the original volume (350 cc.). The pressure, therefore, must decrease to $\frac{350}{400}$ of its original value. Since the temperature is lowered from 313° to 300°C., the pressure will be decreased to $\frac{300}{313}$ of its original value.

Combining these effects, we find that the required pressure is

$$550 \times \frac{350}{400} \times \frac{300}{313} = 461.3 \text{ mm.}$$

PROBLEM 3. At 0°C. and 760-mm. pressure, 1 g. of hydrogen gas occupies a volume of 11.2 liters. Find the volume of 1 g. of hydrogen at 42°C. and 655 mm. The weight of a given quantity of gas does not change when the gas is heated, cooled, or compressed. If we do not add gas molecules or allow any of them to escape, then the volume, temperature, and pressure are the only variables.

<i>Old conditions</i>	<i>New conditions</i>
$P = 760 \text{ mm.}$	$P' = 655 \text{ mm.}$
$V = 11.2 \text{ liters}$	$V' = \text{unknown}$
$T = 273^\circ\text{A.}$	$T' = 315^\circ\text{A.}$

The volume of the sample of hydrogen under the new conditions is

$$11.2 \times \frac{760}{655} \times \frac{315}{273} = 15 \text{ liters.}$$

Knowing that 15 liters of hydrogen under the new conditions weigh 1 g., we are able to find the weight of 1 liter of the gas under these conditions. Weight of 1 liter of hydrogen at 42°C. and 655 mm. is equal to $\frac{1}{15}$ g. = 0.0666 g.

Standard conditions. The chemist is frequently interested in the density of a gas, or the weight of a liter or of a cubic centimeter of the gas. The number of molecules in a liter varies with the pressure and temperature, according to the laws of Boyle and Charles; hence, the density is different for every pressure and temperature. We learned that 1 liter of hydrogen weighs 0.09 g., but that statement really means nothing unless we know the temperature and pressure under which the hydrogen was measured. Scientists have agreed, in order to have uniformity, to measure the densities of gases under certain *standard conditions*, or to correct them to these conditions. A temperature of 0°C. has been chosen as the *standard temperature*, and one atmosphere, the average pressure of the air at sea level, as the *standard pressure*. When we say that hydrogen has a density of 0.09 g. per liter, we mean that it has this density at 0°C. and under a pressure of 1 atmosphere (76 cm. = 760 mm. of mercury).

Correction for pressure of water vapor. We often collect gases in the laboratory by the displacement of water. Since water vaporizes readily, this means that the gas is wet—that is, the bottle or tube contains some water molecules as well as gas molecules. Does the presence of these water molecules make a difference in the volume and pressure of the gas?

We can answer this question by performing a simple experiment with our barometer tube. A little air is introduced under the opening of the tube while the open end of the tube is immersed in mercury. Immediately the top of the column of mercury falls to a lower position. If, now, a drop of water is placed under the mouth of the tube and allowed to rise through the column of mercury as the air bubbles did, some of the water vaporizes, and the level of the mercury falls to a still lower position. The gas and water molecules are now both tending to drive the mercury out of the barometer tube.

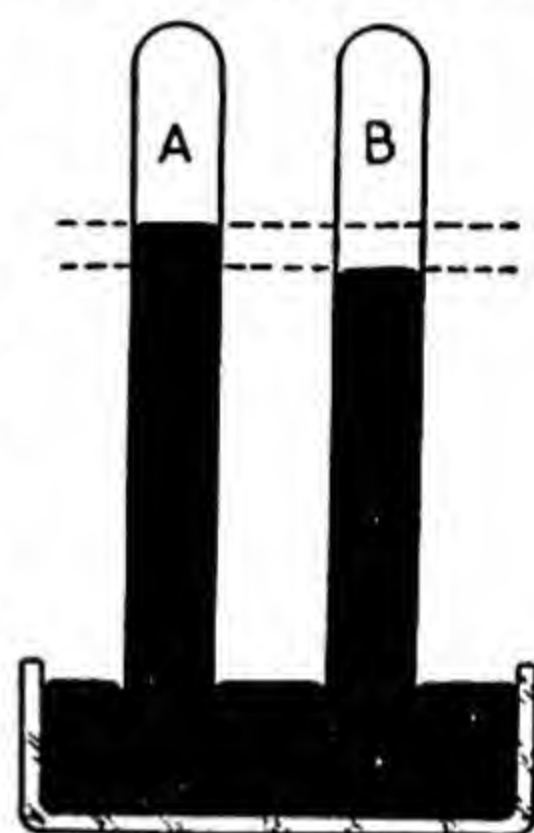


Fig. 61. Barometer tubes; A, with dry air above the mercury; B, with moist air above the mercury.

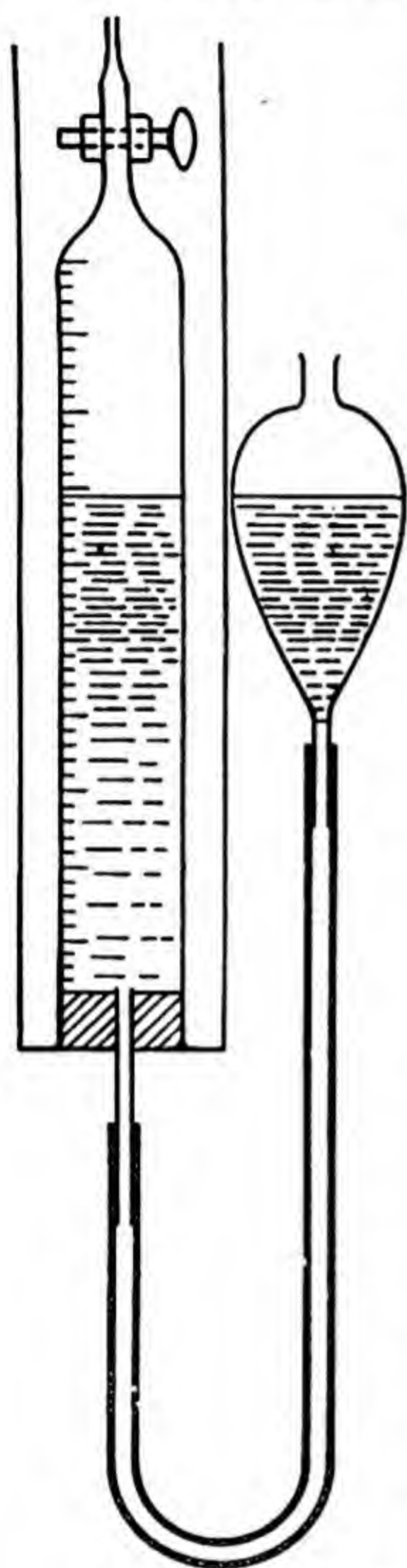


Fig. 62. A convenient device for measuring the volume of a gas. The gas is confined in the inverted burette. The space between the burette and the outer jacket is filled with water or an oil which may be maintained at any desired temperature. Mercury is used in the burette and the leveling bulb when dry gases are to be measured.

reading 762 mm.,

We see that the presence of water vapor in a gas increases either the volume or the pressure of the gas. There are actually two gases present, each occupying a certain volume and exerting a definite pressure. The total volume is equal to the sum of the volumes of the two gases. At any given temperature each gas in a mixture maintains its energy of motion (kinetic energy) no matter how many kinds of gas molecules the mixture contains. The pressure of a gas is due to impacts of the gas molecules on the walls of the vessel in which the gas is confined, and the pressure due to a particular gas is the same regardless of the presence or absence of other kinds of gases. The total pressure in a mixture of gases equals the sum of the partial pressures of the individual gases present. Likewise, the total volume is equal to the sum of the volumes of the various gases present. This generalization is Dalton's law.

When a gas is collected over water it is mixed with water vapor which, in turn, is in equilibrium with water in the liquid state, and the partial pressure of the water vapor is dependent only upon the temperature. (See page 69.) The table on page 513 shows the vapor pressure of water in millimeters of mercury over a range of temperatures.

EXAMPLE 1. Let us suppose that we have collected a quantity of hydrogen over water and that we have measured its volume under atmospheric pressure. Let us determine what volume the hydrogen would occupy if it were free from water vapor.

The pressure exerted by the hydrogen gas plus the pressure exerted by the water vapor which is mixed with the hydrogen is equal to atmospheric pressure. Expressing this fact in the form of an equation, we have

$$P_{\text{atmosphere}} = P_{\text{H}_2} + P_{\text{water vapor}}. \quad (1)$$

Let us assume that the volume of the mixed gases (hydrogen plus water vapor) is 50 cc., the barometric reading 762 mm., and the temperature 25°C. The vapor pressure of

water at 25°C. is 23.5 mm. We now have all the data necessary for the solution of our problem.

We first find the pressure which the hydrogen alone is exerting by transposing equation 1:

$$P_{\text{atmosphere}} - P_{\text{water vapor}} = P_{\text{H}_2}$$

or

$$762 - 23.5 = 738.5 \text{ mm.}$$

<i>Original conditions</i>	<i>Final conditions</i>
$P = 738.5 \text{ mm.}$	$P' = 762 \text{ mm.}$
$V = 50 \text{ cc.}$	$V' = \text{unknown}$
$T = 25^\circ + 273^\circ = 298^\circ\text{A.}$	$T' = 298^\circ\text{A.}$

The temperature is the same throughout the experiment; so it does not enter into the calculation. The volume which the dry gas would occupy under an atmospheric pressure of 762 mm. is

$$50 \times \frac{738.5}{762} = 48.4 \text{ cc.}$$

Graham's law. Gases, when mixed, become uniformly distributed in the container. Each gas fills the entire space and exerts its own pressure as if the other gases were not present. This rule applies to all gases which do not react with each other to form compounds. The rate at which a gas mixes with other gases or diffuses through a porous wall is determined mainly by its density. At the same temperature and pressure, light gases diffuse faster than do heavy gases. If a bottle containing hydrogen and oxygen is opened at one end of a room, hydrogen molecules from the bottle will reach the opposite end of the room in one-fourth the time required for oxygen molecules to travel the same distance. If methane gas and sulfur dioxide gas are placed under the same pressure in similar vessels made of unglazed porcelain, the methane will diffuse through the porous walls of its container twice as fast as the sulfur dioxide.

Graham discovered that *the rates of diffusion of gases are inversely proportional to the square roots of their densities.*

The densities of *gases* (weights per liter) are proportional to their molecular weights, for equal volumes of gases contain the same number of molecules. We may, therefore, compare the rates of diffusion of gases by comparing the square roots of their molecular weights, or we may compare the square roots of their weights per liter. For example: the molecular weight of hydrogen is 2 and of oxygen, 32. The ratio is $\frac{2}{32}$ or $\frac{1}{16}$. The square roots of these relative weights are 1 and 4. Since the rates of diffusion are

inversely proportional to these numbers we see that hydrogen diffuses four times as fast as does oxygen.

The weight of a liter of methane is 0.715 and the weight of a liter of sulfur dioxide is 2.86. The ratio is $\frac{0.715}{2.86}$ or $\frac{1}{4}$, and we have $\frac{\sqrt{1}}{\sqrt{4}} = \frac{1}{2}$. Methane, then, diffuses twice as fast as does sulfur dioxide.

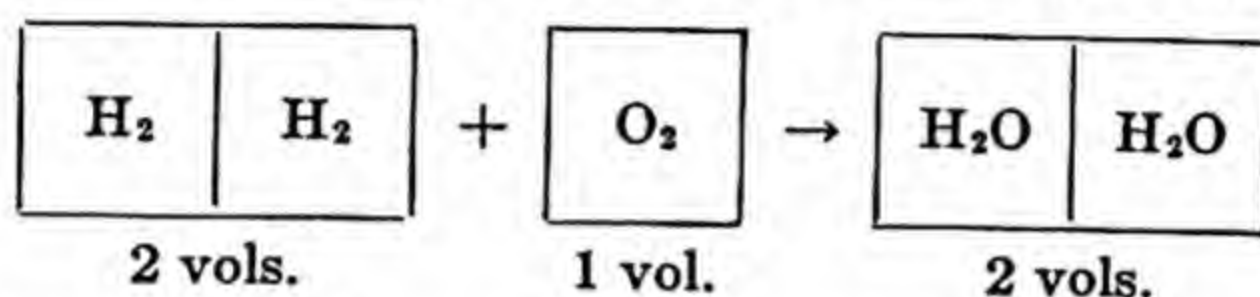
Questions and Exercises

1. What is the volume of 1 g. of oxygen at 0°C. and 1 atmosphere of pressure? What volume will it occupy at 20°C. and 1 atmosphere?
2. If the gas in a sealed container exerts a pressure of 70 cm. at 0°C., what pressure will it exert at 100°C.?
3. What is the volume of one mole of any gas at 100°C. and 760 mm. pressure?
4. What is the volume in cubic centimeters occupied by 1 g. of hydrogen at 20°C. and 750 mm. pressure?
5. What would be the volume, at 0°C. and 760 mm., of a gas which occupied 300 cc. at 50°C. and 750 mm. pressure?
6. If 3 g. of a gas exerts a pressure of 760 mm. when held in a certain container, what weight of the same gas is required to exert a pressure of 1000 mm. in the same vessel at the same temperature?
7. A vessel having a capacity of 620 cc. is filled with oxygen under a pressure of 720 mm. at 17°C. What is the weight of gas in the container?
8. What volume of carbon dioxide measured at 22°C. and 665 mm. can be obtained from 50 g. of sodium carbonate and an excess of hydrochloric acid?
9. What volume of oxygen at 150°C. and 720 mm. can be obtained by heating 75 g. of potassium chlorate?
10. What pressure must be applied to force 4 g. of carbon dioxide at 20°C. into a cylinder that has a capacity of 1 liter? (*Note:* First find the volume occupied by 4 g. of the gas under standard conditions; then find the pressure necessary to change this volume to 1 liter at 293°A.)
11. A vessel having a capacity of 400 cc. is filled with hydrogen under standard conditions (0°C. and 760 mm.). The vessel is then heated to 10°C. Must the gas be allowed to escape or must more gas be pumped into the vessel to make the pressure of the gas 765 mm.? What weight of hydrogen must be added or removed to make the pressure 760 mm. at 10°C.?
12. How much more gas can be obtained by measuring a gas in a meter at -10°C. than by measuring it at +30°C.? Write the answer in the form of a fraction.
13. Compare the rates of diffusion of the following gases: (a) CH₄ and SO₂, (b) H₂ and CO₂, (c) He and HCl, (d) NH₃ and N₂.
14. A certain gas occupies a volume of 10 liters under a pressure of 1 atmosphere. What volume will it occupy under a pressure of (a) $\frac{1}{3}$ atmosphere; (b) 10 atmospheres; (c) $\frac{1}{10}$ atmosphere; (d) 100 atmospheres? Assume constant temperature.

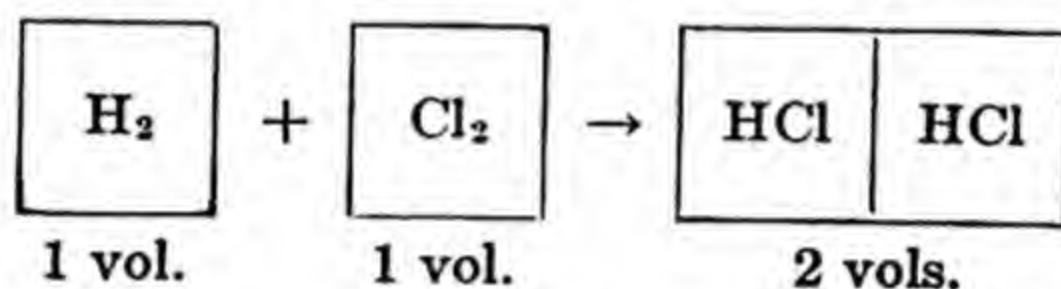
PART 7

Gay-Lussac's Law; Avogadro's Law

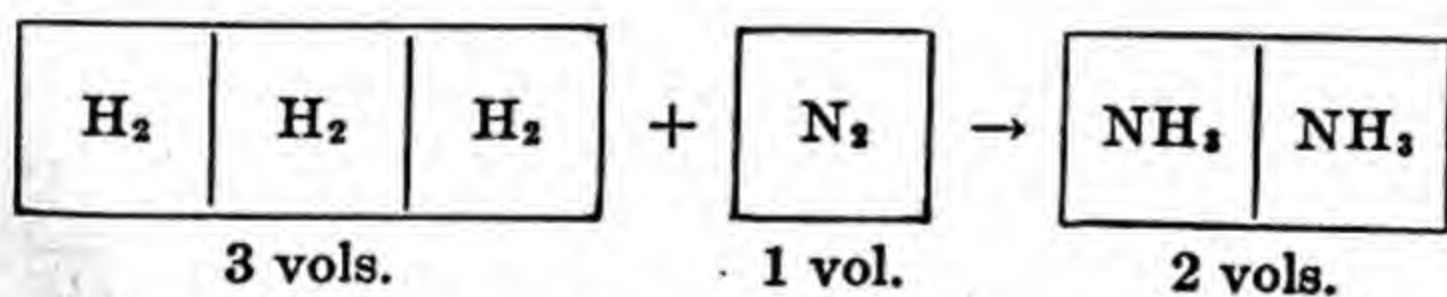
Volume relations of gases. When hydrogen and oxygen combine to form steam, or gaseous water, *2 volumes* of hydrogen unite with *1 volume* of oxygen to form *2 volumes* of steam:



Experiments prove that *1 volume* of hydrogen unites with *1 volume* of chlorine to form *2 volumes* of hydrogen chloride:



When hydrogen and nitrogen form ammonia gas, *3 volumes* of hydrogen unite with *1 volume* of nitrogen, producing *2 volumes* of ammonia, NH₃:



Gay-Lussac's law. Gay-Lussac noticed that in these reactions the volumes of the gases are all expressed in small whole numbers. He wondered whether all gases react in this simple manner. He studied many gaseous reactions, and in 1808 concluded that: *When gases react, their relative combining volumes and the volume of the product, if it is a gas, can be expressed by small whole numbers.* Since no exceptions to this statement have been found, Gay-Lussac's rule is accepted by scientists as a law of nature.

Avogadro's law. Avogadro, an Italian scientist, was also interested in the uniform behavior of gases. More than a century ago, in 1811, he concluded from his studies of gaseous reactions that *equal volumes of gases, at the same temperature and pressure, contain the same number of molecules.*

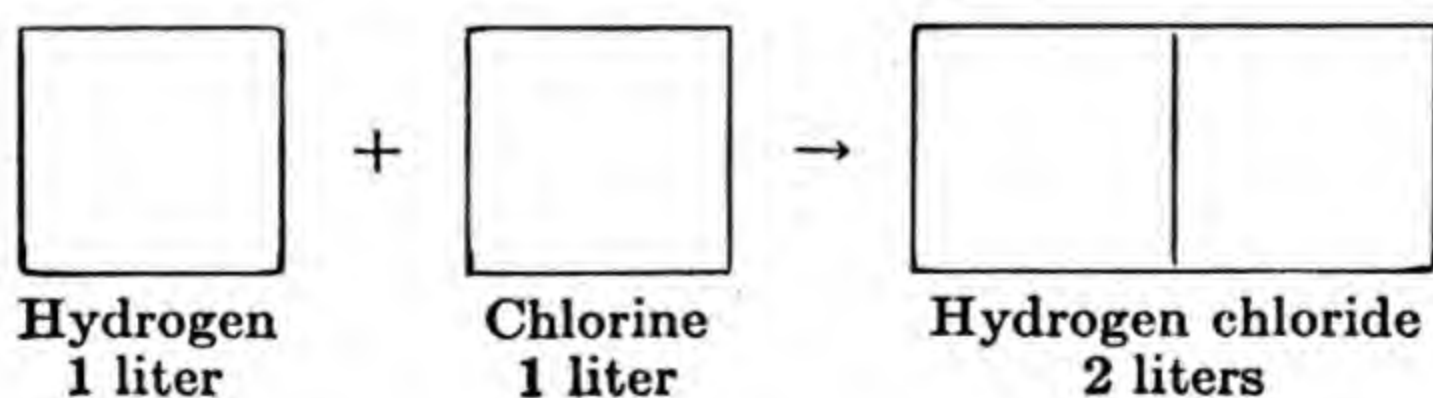
This law means that a bottle of oxygen contains the same number of molecules as an identical bottle filled with hydrogen, carbon dioxide, or any other gas. Since that time many other noted scientists, including Perrin, Rutherford, and Millikan, have been able to estimate the actual number of molecules in a given volume of a gas, and they have concluded that there are approximately 27,000,000,000,000,000,000,000 molecules in one liter of any gas under standard conditions. This number is conveniently written 27×10^{21} or 2.7×10^{22} .

We can use Avogadro's law to prove a statement which was made in an earlier chapter; namely, that the molecules of the common gaseous elements contain two atoms in the molecule.

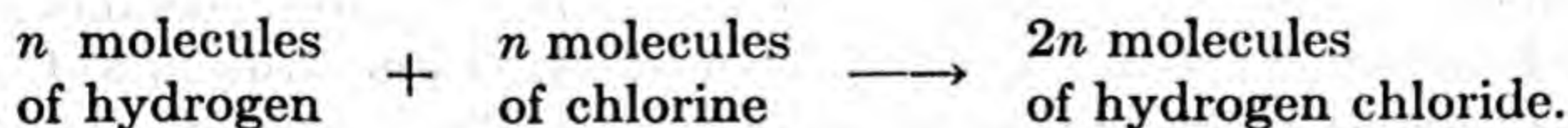
The hydrogen molecule. We have been writing the formula for hydrogen gas as H_2 . Why do we think that the hydrogen molecule is composed of two atoms, and is not monatomic, as are molecules of helium, neon, and argon?

Let us consider the synthesis of hydrogen chloride. We know from experiment that 1 liter of hydrogen combines with 1 liter of chlorine to form 2 liters of hydrogen chloride. From Avogadro's law we know that we have the same number of molecules of hydrogen in a liter of hydrogen gas as there are molecules of chlorine in a liter of chlorine gas.

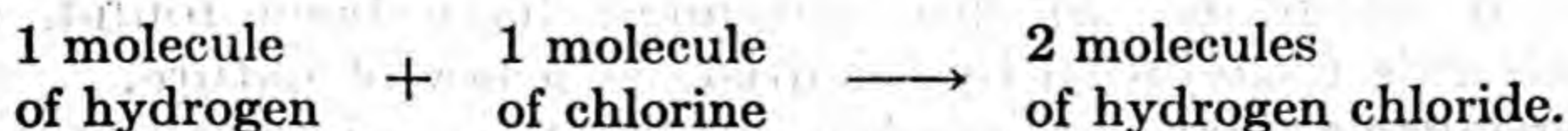
Let us represent this large number of molecules in 1 liter of a gas by the letter n . Then 1 liter of hydrogen and 1 liter of chlorine each contain n molecules, and there must be $2n$ molecules in the two liters of hydrogen chloride formed (n molecules in each liter):



or

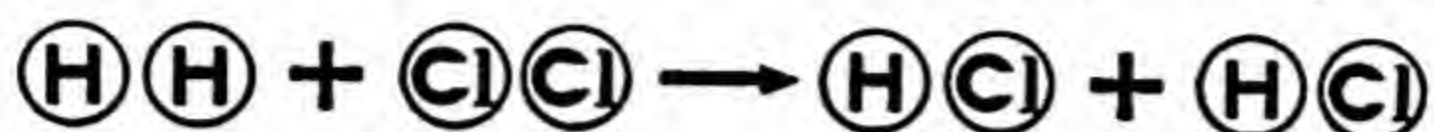


Dividing both sides of the last equation by n , we have



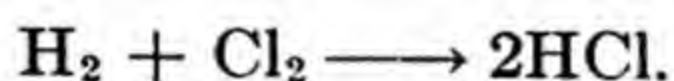
Every molecule of hydrogen chloride must contain at least one hydrogen atom. Two molecules of hydrogen chloride must, then, contain at least two atoms of hydrogen, but these two molecules were formed from *one* molecule of hydrogen. Hence the

molecule of hydrogen must have been composed of two atoms of hydrogen. The reaction is represented graphically as follows:

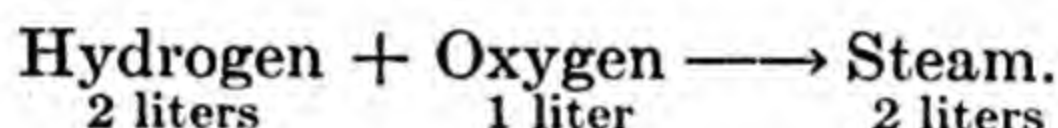


It should be noticed that any *even* number might have been used instead of 2. However, no chemical reaction is known in which the hydrogen molecule splits into more than two parts. The formula for hydrogen gas, therefore, is written H_2 .

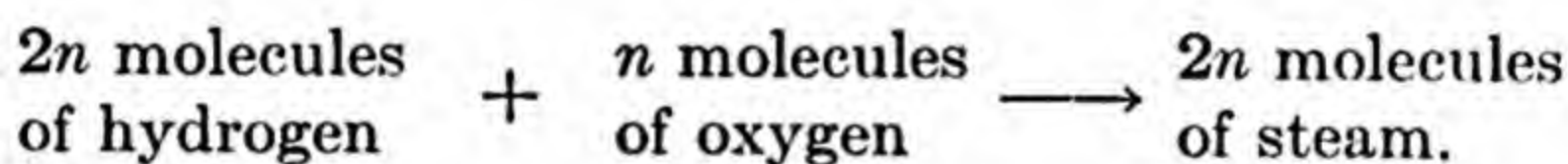
The chlorine molecule. We can prove from the same experiment that the chlorine molecule contains two chlorine atoms. The formula for the chlorine molecule, therefore, is Cl_2 . Since one molecule of hydrogen and one molecule of chlorine react to form two molecules of hydrogen chloride, the formula for the latter must be HCl , and the correct equation for the reaction between hydrogen and chlorine gas is written



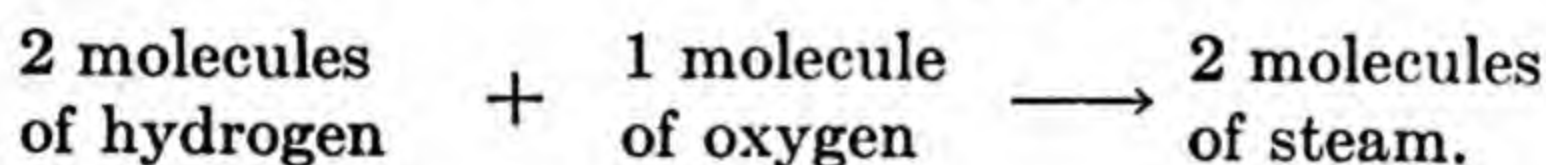
The oxygen molecule. The volume equation for the union of hydrogen and oxygen proves that the formula for oxygen gas is O_2 :



or



Dividing both sides of the equation by n , we have



Each molecule of steam, or hydrogen oxide, must contain at least one oxygen atom. The two molecules therefore contain at least two oxygen atoms. These came from *one* molecule of oxygen. An oxygen molecule, therefore, is composed of an even number of atoms of oxygen, and, since there is no evidence that an oxygen molecule ever divides into more than two parts, the formula is written O_2 .

The acceptance of Avogadro's view that, under similar conditions of temperature and pressure, the molecules of one gas occupy the same volume as the same number of molecules of any other gas, gives us a complete explanation of the fact that gases combine in simple proportions by volume. A simple ratio exists between the numbers of molecules that take part in a chemical reaction, and the same ratio exists between the volumes of the reacting gases.

Questions and Exercises

1. State Gay-Lussac's law.
2. State Avogadro's law.
3. Prove that the molecule of chlorine gas consists of an even number of chlorine atoms.
4. From the reaction between nitrogen and hydrogen, forming ammonia gas, prove that the correct formula for nitrogen is N_2 .
5. Two volumes of nitric oxide give 1 volume of nitrogen and 1 volume of oxygen when decomposed. Prove from this fact that the formula for oxygen is O_2 , and that the formula for nitrogen is N_2 .
6. What is the smallest number of hydrogen atoms that can be present in 1000 molecules of hydrogen chloride? How many hydrogen molecules are needed to furnish these hydrogen atoms?
7. What is the smallest number of oxygen atoms that can be present in 500 molecules of steam? How many oxygen molecules would have to burn with hydrogen to make 500 molecules of steam?
8. Show that Gay-Lussac's law would lead us to expect that there would be some oxygen left if we tried to make 1.1 liters of oxygen combine with 2 liters of hydrogen.
9. It requires 2 liters of oxygen to burn 1 liter of methane gas completely. How many molecules of oxygen are required for the combustion of 1 molecule of methane?
10. Three volumes of oxygen produce two volumes of ozone. If the formula for oxygen is O_2 , what is the correct formula for ozone?
11. Two molecules of nitric oxide react with one molecule of oxygen to produce two molecules of nitrogen dioxide. How many liters of oxygen are required to react with 2 liters of nitric oxide?

UNIT III

Atoms; Molecules; the Electron Theory; the Periodic Table

PART 1

Atoms; Atomic Weights; Molecular Weights

Why we believe that atoms exist. We have spoken freely about atoms without giving any reasons for believing that they exist. Just why does the chemist think that everything is made of tiny particles of definite sizes and weights?

The first reason for his belief in atoms is the law of definite proportions—the fact that a compound always contains exactly the same relative weights of its constituents. For example, if a crystal of salt (sodium chloride) is decomposed into its elements, we find that the sodium and chlorine are present in the proportion of 23 parts of sodium to 35.5 parts of chlorine. It makes no difference how large a piece of sodium chloride is decomposed or from what source it is obtained, as long as it is pure. It may be obtained by the evaporation of sea water, or it may be taken from a salt bed in a desert, or it may be made from the elements in the laboratory. The ratio of the weights of sodium and chlorine is always 23 to 35.5.

The only explanation which can be offered for this fact is that sodium chloride is made of units of matter which have definite weights. These tiny particles are called atoms. In the vapor state sodium chloride exists in the form of separate molecules each of which is composed of an atom of sodium of definite weight and an atom of chlorine of definite weight, and the relative weights of these atoms are 23 and 35.5. The same ratio is found in solid salt, which shows that the crystal is composed of equal numbers of sodium and chlorine atoms. An atom of chlorine weighs about one and a half times as much as an atom of sodium. When 1000 molecules of sodium chloride are decomposed, 1000 sodium atoms and 1000 chlorine atoms are obtained. The weights of sodium

and chlorine obtained from these 1000 molecules are still in the ratio of 23 to 35.5.

When hydrogen combines with chlorine to form hydrogen chloride, we find, upon analysis, that there is always a definite ratio between the weight of hydrogen and the weight of chlorine in the compound. This ratio is 1 part of hydrogen to 35.5 parts of chlorine. Hence, hydrogen chloride must be composed of atoms of hydrogen of definite weight and of atoms of chlorine, likewise of definite weight, and the chlorine atom must weigh 35.5 times as much as the hydrogen atom.

The second reason for believing in the existence of atoms is the law of multiple proportions. For example, in the two compounds carbon monoxide and carbon dioxide, analysis proves that there is always exactly *twice* as much oxygen combined with a given weight of carbon in the dioxide as in the monoxide. This can be true only if the particles of oxygen which combine with carbon particles are all of the same size and weight, and if twice as many of them have combined with the same weight of carbon in the second oxide as in the first one.

Atomic weights. Chemists have analyzed thousands of compounds and have found the ratio of the weights of the atoms making up each compound. From these data they have determined what is called the atomic weight of each element. Hydrogen is the lightest atom that has been discovered, and it would be logical to assign to hydrogen the atomic weight of 1 and then use this weight of the hydrogen atom as the basis for calculating all others. Actually it is simpler to use the oxygen atom as a basis of comparison, for nearly all elements can be made to combine with oxygen. For the purpose of comparison, oxygen is assigned an atomic weight of exactly 16.

If we adopt the value of exactly 16 for oxygen, the atomic weight of hydrogen becomes 1.008. This, however, is so close to an atomic weight of 1 that we may for practical purposes call the atomic weight of hydrogen 1 and of oxygen 16, and we may use either hydrogen or oxygen as a basis for comparison in determining the atomic weights of the other elements. The actual weight of a hydrogen atom is a very small number. It takes 300,000,000,000,000,000,000,000 hydrogen atoms to weigh one gram. A five-cent piece weighs about 5 g. Since chlorine atoms combine with hydrogen atoms in the ratio of 35.5 to 1, and chemists have reason to believe that a hydrogen chloride molecule is composed of one hydrogen atom holding one chlorine atom, 35.5 is taken as the

weight of the chlorine atom. The atomic weight of sodium is 23, from the results of the analysis of sodium chloride. We found that the ratio of the weights of hydrogen and oxygen in water is 1 to 8, and at first glance we might conclude that the atomic weight of oxygen is 8. However, it is known from other experimental evidence that the molecule of water is made of *two* atoms of hydrogen and *one* atom of oxygen, which makes the oxygen atom 8 times as heavy as two hydrogen atoms, or 16 times as heavy as one hydrogen atom. The atomic weight of oxygen, therefore, is 16.

The exact atomic weights of the elements are included in the table on the back cover of the book. The atomic weights of some of the commoner elements are given in the following table. The atomic weight in each case states merely how much the atom weighs in comparison with the weight of the atom of hydrogen, or the weight of the atom as compared with the weight of an oxygen atom, the latter being assigned the value of 16.

ATOMIC WEIGHTS OF SOME COMMON ELEMENTS			
Hydrogen.....	1	Chlorine.....	35.5
Oxygen.....	16	Iron.....	56
Nitrogen.....	14	Calcium.....	40
Carbon.....	12	Sulfur.....	32
Helium.....	4	Magnesium.....	24

Molecular weights. The molecular weight of an element or of a compound is the weight of its molecule in terms of the weight of an atom of hydrogen. It is determined by adding the atomic weights of the atoms which make up the molecule. The weight of a molecule of sodium chloride is $23 + 35.5$, or 58.5. This is the molecular weight of sodium chloride. The molecular weight of water is 18, that is, $(2 \times 1) + 16$; that of hydrogen gas is 2, that is, 2×1 ; and that of oxygen is 32, or 2×16 .

Questions and Exercises

1. What is meant by the term "atomic weight"?
2. What is meant by the term "molecular weight" as applied to an element or a compound?
3. Would it be appropriate to speak of the "atomic weight" of a compound? Explain.
4. Why do we believe that all matter exists in the form of atoms?
5. Calculate the molecular weight of cane sugar. The sugar molecule consists of 12 carbon atoms, 22 hydrogen atoms, and 11 oxygen atoms. Its formula is written $C_{12}H_{22}O_{11}$.

6. Complete the following table:

Name of element	Atomic weight	Number of atoms in the molecule	Molecular weight
Oxygen.....			
Hydrogen.....			
Argon.....			
Nitrogen.....			
Neon.....			
Chlorine.....			
Helium.....			

PART 2

The Electron Theory

We no longer believe, as Dalton did, that the atom is the smallest thing in existence, that it is indivisible, or that all atoms of the same element have exactly the same mass. We know, however, that all atoms of the same element have similar chemical properties, and that atoms of different elements have different chemical properties.

Chemists have thought about atoms for a long time. They have tried to answer questions like these: What causes the differences between the properties of different atoms? Of what material is an atom actually made? What causes atoms to combine with other atoms to form compounds?

Stars differ in composition. Toward the end of the nineteenth century a series of discoveries occurred in relatively rapid succession that answered some of these questions and gave us a new idea of the structure of matter. Astronomers observed that the hottest stars are composed of a few simple gases like hydrogen and helium; that cooler stars contain a dozen or more elements, while still older and cooler stars have most of the elements that are found on the earth. The spectroscope makes it possible to identify the atoms in the atmospheres of the sun and the stars. The earth, as we know, contains 92 different elements. Since the hottest stars contain fewer elements than are found in the cooler ones, the number of elements must increase in some manner as a star grows old and becomes cooler. Is it possible for the simpler elements like hydrogen and helium to combine and form the heavier elements? Recent discoveries lead to this conclusion.

The discovery of uranium. In 1896 Becquerel, a French chemist, discovered that the element uranium has properties different from those of any element which had been previously discovered. When a piece of uranium was placed in a dark room near a photographic plate, the plate was affected as if it had been exposed to sunlight. Scientists all over the world were astounded by this action. They began to study the properties of uranium, especially as to why it affects a photographic plate. They discovered that the atoms of the element explode spontaneously,

shooting off positively charged helium atoms (*helium ions*), negatively charged electrical particles called *electrons*, and gamma rays. The latter are very much like X-rays. The helium ions and the electrons are ejected from an exploding atom of uranium with enormous velocities. Such projectiles have great penetrating power.

Chemists are unable to control the explosion of uranium in any way. Normal chemical reactions increase in speed when the temperature is increased; usually an increase of 10° doubles the speed of a reaction. Cooling makes most reactions go more slowly. The decomposition of uranium, however, proceeds at the same speed whether the temperature is increased several hundred degrees or lowered to the temperature of liquid air.

The Curies discover radium. While carrying on investigations with uranium ore, Pierre Curie and his wife, Marie, isolated a substance which is about a million times more active than uranium. They named this element radium. Radium is one of the decomposition products of uranium. In other words, when an atom of uranium explodes, giving off helium gas and electrons, the remainder of the uranium atom is found to be an atom of a different element. Some elements, therefore, can change spontaneously into other elements.

Radium, like uranium, decomposes spontaneously, changing into helium and other elements. Chemists and physicists reasoned that if certain elements *spontaneously* change into other elements, perhaps methods could be found to make other elements undergo similar changes. This induced transmutation has been accomplished recently with the aid of an instrument called the cyclotron. Scientists have succeeded both in forming lighter elements from heavier ones (nitrogen from oxygen) and in building up heavier elements from lighter ones (magnesium from sodium). We no longer believe that the atom is indivisible, but that it is a little bundle of electrical energy or of tiny, electrically charged particles. How are these particles put together to make an atom, and what is the difference in structure between the atoms of different elements?

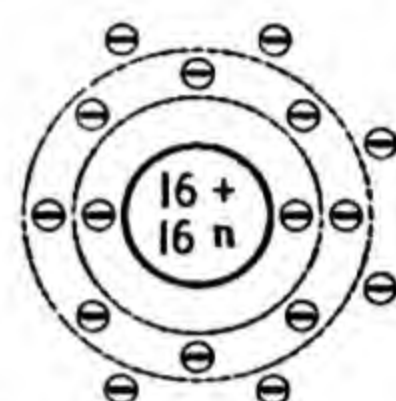
The nucleus. Every atom has a central portion called the nucleus which is positively charged. The nucleus is never disturbed in any chemical reaction, but is affected in radioactive decompositions, and by bombardment with swiftly moving particles produced in a cyclotron. Practically all of the weight of the atom is associated with the nucleus.

The nucleus of an atom (with the exception of the hydrogen atom) contains both positively charged particles called *protons*

and uncharged particles called *neutrons*. A neutron has approximately the same mass as a proton, but it has no electrical charge.

Electrons and electron shells. An electron is a tiny particle of negative electrical energy about $\frac{1}{1845}$ as heavy as a hydrogen atom. The negative charge of an electron is equal in magnitude to the positive charge of a proton. The weight of an electron is negligible in comparison with that of a proton or of a neutron, so we may disregard the electrons when we talk about the weight of an atom. For all practical purposes the weight of the nucleus

Fig. 63. Electron orbits. One method of representing the positions of electrons in the first, second, and third shells.



is the weight of the atom, for the nucleus contains all the protons and neutrons of the atom. In other words, the atomic weight of an element is the sum of the weights of the protons and neutrons in the nucleus of an atom of that element. Although the nucleus of every atom is positively charged, the atom as a whole is electrically neutral, for the nucleus is surrounded by electrons, equal in number to the protons in the nucleus. A Danish scientist, Niels Bohr, developed the theory that the electrons revolve around the nucleus in orbits, in the same way that the planets of the solar system revolve around the sun. We now believe that these tiny, elec-



From Herzberg, "Atomic Spectra and Atomic Structure"

Fig. 64. Another method of representing the positions of electrons in the first, second, and third shells.

trically charged particles—the electrons—are moving around the nucleus of the atom, not in perfectly regular orbits, but in paths that are subject to continuous change. Instead of representing electrons in definite positions in a regular orbit, as in Fig. 63, we should, perhaps, say that these electrons are somewhere within the broadened band shown in Fig. 64. The position of this fuzzy band does not always remain as represented in the plane of the printed page, but can itself rotate. On this account it is better to refer to the electrons as forming shells around the nucleus instead of referring to them as moving in fixed orbits. We shall,

however, use the terms "shells" and "orbits" interchangeably, for both terms are in common use in the chemical literature, and we shall use the simple orbits in all our pictures of the atoms.

Atomic number. Moseley, a brilliant English physicist, discovered that by X-ray experiments he could determine the charge on the nucleus of any atom. This charge is equal to the number of protons in the nucleus and equal also to the number of electrons in the orbits surrounding the nucleus. As a result of Moseley's work, it is possible to arrange the atoms in the order of their atomic numbers. The *atomic number* of an element is equal to the number of positive charges in the nucleus—that is, the number of protons in the nucleus. It is equal also to the number of electrons surrounding the nucleus. The *atomic weight* of an element corresponds to the sum of the protons and neutrons in the nucleus of the atom. A few of the elements are arranged in the order of their atomic numbers in the table below.

ELEMENTS ARRANGED IN THE ORDER OF THEIR ATOMIC NUMBERS

Element	Atomic number	Atomic weight
Hydrogen.....	1	1
Helium.....	2	4
Lithium.....	3	7
Beryllium.....	4	9
Boron.....	5	11
Carbon.....	6	12

We see that if hydrogen is assigned the number 1, the atomic number of helium becomes 2, lithium 3, and so on.

The Nucleus and the Arrangement of the Electrons in the Orbits Surrounding the Nucleus

The hydrogen atom. The lightest of all atoms, the hydrogen atom, has been assigned the atomic number 1. Its atomic weight



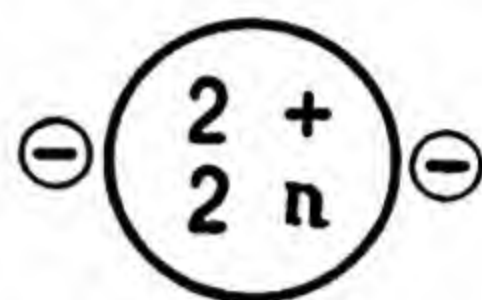
Fig. 65. The hydrogen atom. One proton in the nucleus. One electron outside the nucleus. Atomic number, 1. Atomic weight, 1.

also is 1, since its nucleus consists of a single proton. There is one electron in an orbit surrounding the nucleus. The atom as a whole is uncharged, since the positive charge of the nucleus is neutralized by the negative charge of the electron outside the

nucleus. In the drawings showing the structures of the atoms we shall represent a proton by a plus (+) sign, an electron by a minus (—) sign, and a neutron by the letter *n*.

The helium atom. Helium has the atomic number 2, and an atomic weight of 4. It has two protons and two neutrons in the

Fig. 66. The helium atom. Two protons and two neutrons in the nucleus. Atomic number, 2. Atomic weight, 4.



nucleus, and two electrons outside the nucleus. Both the electrons which are outside the nucleus are in the same shell. The first shell around the nucleus of an atom never holds more than two electrons.

The lithium atom. Lithium has the atomic number 3, and an atomic weight of 7. There is a charge of +3 on the nucleus, and there are three electrons outside the nucleus. Since it is seven times as heavy as a hydrogen atom, the sum of the protons

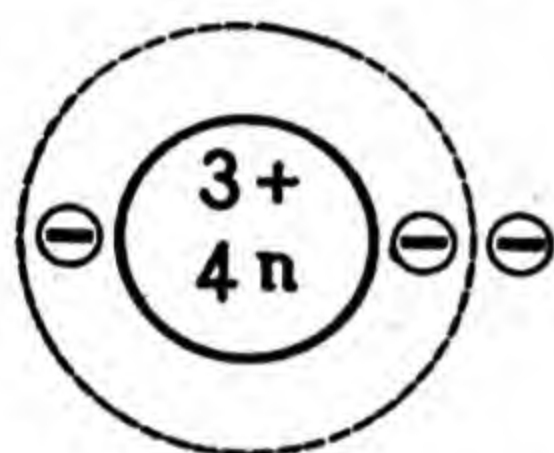


Fig. 67. The lithium atom. Three protons and four neutrons in the nucleus. Atomic number, 3. Atomic weight, 7.

and neutrons in the nucleus is seven. The +3 charge shows that there are three protons in the nucleus of the atom, and the total weight of seven indicates that there are four neutrons there. Since the first electron shell always has two electrons, the third electron must be in a second shell.

The beryllium atom. With an atomic number of 4 and an atomic weight of 9, the beryllium atom is shown in Fig. 68. The third and fourth electrons take their places in the second shell.

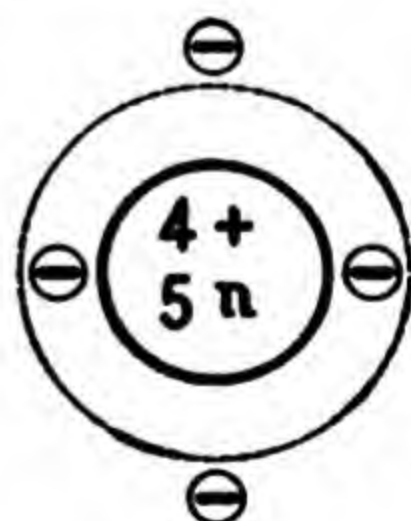


Fig. 68. The beryllium atom. Four protons and five neutrons in the nucleus. Atomic number, 4. Atomic weight, 9.

The next six atoms in the table of atomic numbers—boron, carbon, nitrogen, oxygen, fluorine, and neon—are represented by Figures 69–74.

The second shell in any atom is large enough to hold eight electrons but no more; hence neon has its second shell as well as its first completely filled. Each element has one more proton in the nucleus and one more electron outside the nucleus than the

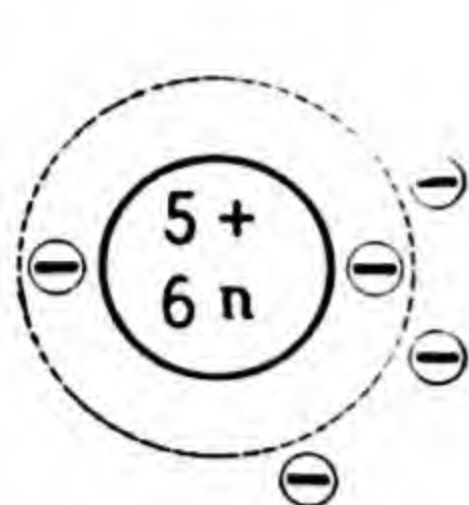


Fig. 69. The boron atom.

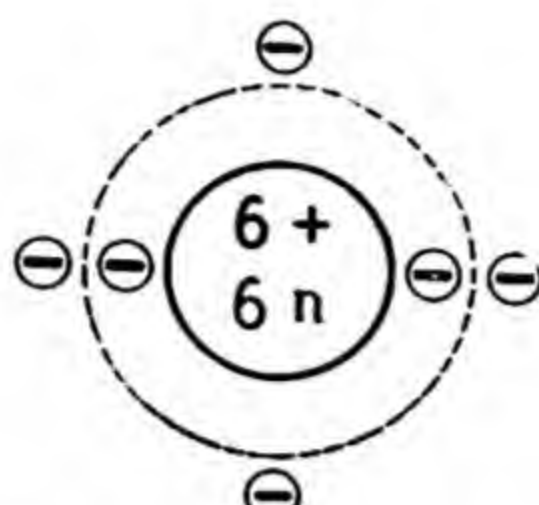


Fig. 70. The carbon atom.

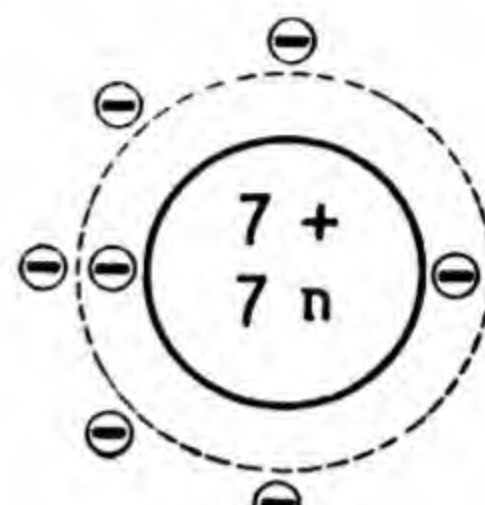


Fig. 71. The nitrogen atom.

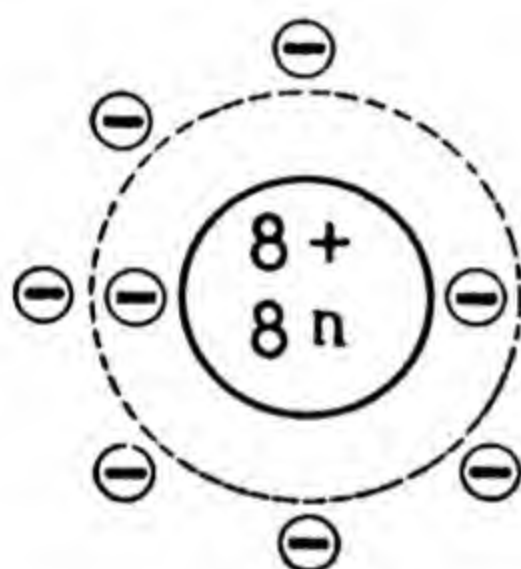


Fig. 72. The oxygen atom.

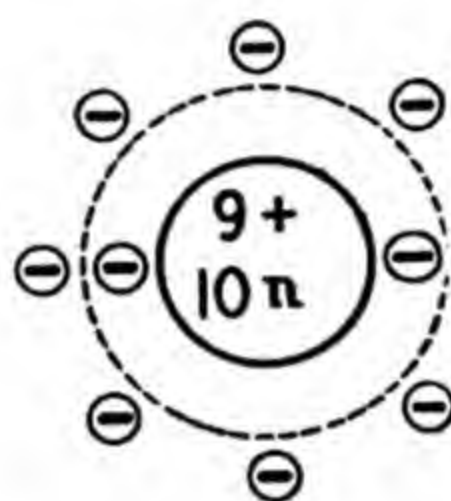


Fig. 73. The fluorine atom.

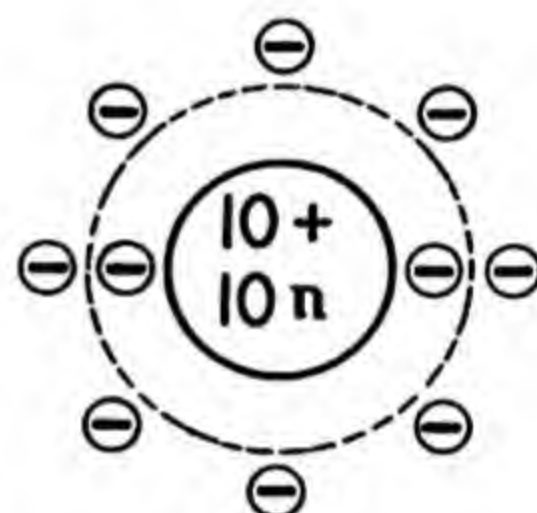


Fig. 74. The neon atom.

preceding one. We should expect, therefore, to find in the next element beyond neon—that is, sodium—an electron in a third shell. Such is the case. Figures 75–82 are pictures of the next eight elements in the order of their atomic numbers. These

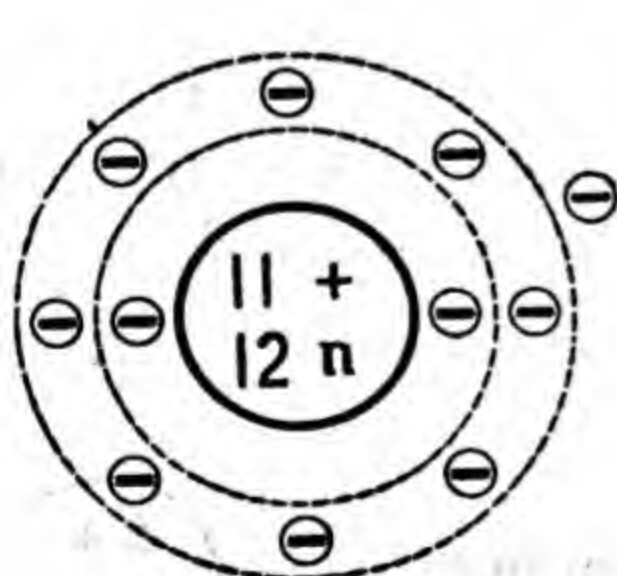


Fig. 75. The sodium atom.

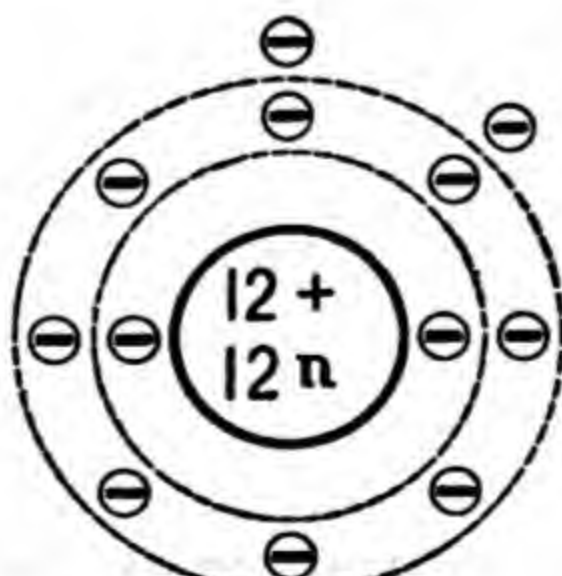


Fig. 76. The magnesium atom.

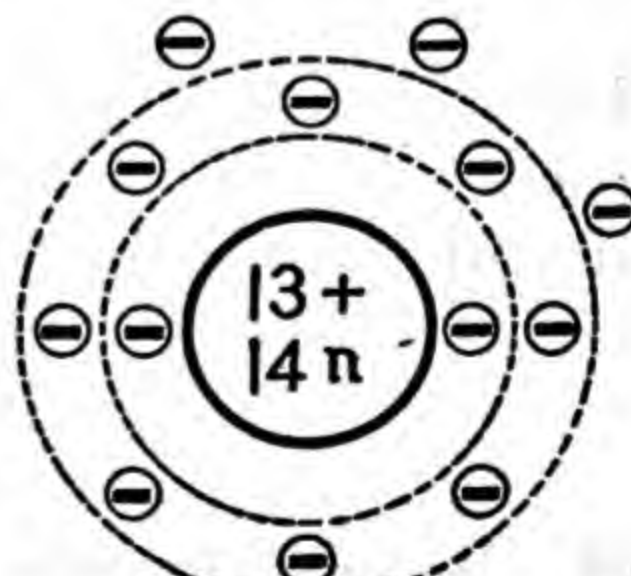


Fig. 77. The aluminum atom.

elements are sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, and argon.

Potassium, with an atomic number of 19, has three electron shells filled, and it has one electron in the fourth shell. Calcium has two electrons in the fourth shell.

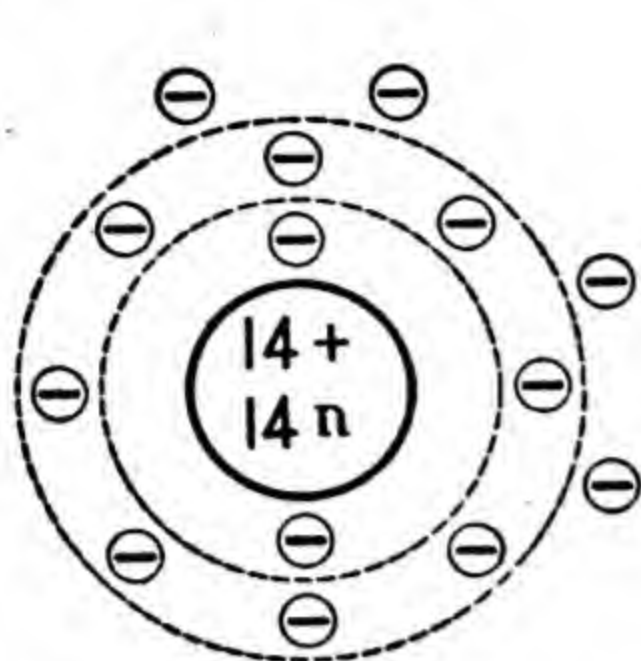


Fig. 78. The silicon atom.

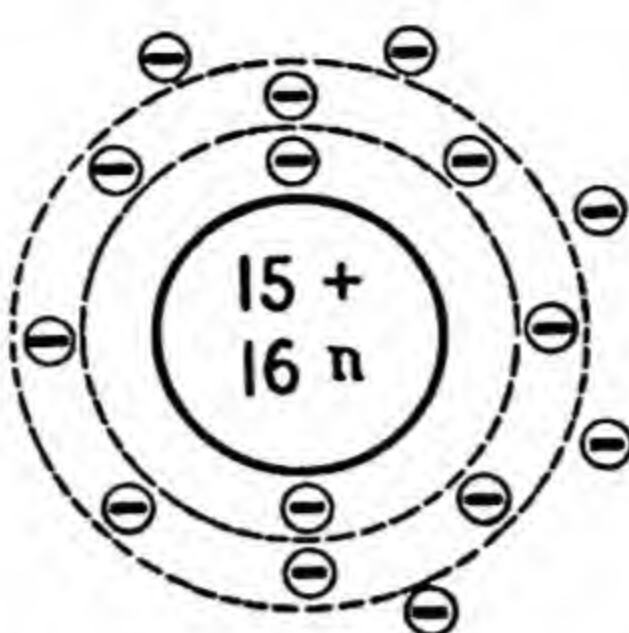


Fig. 79. The phosphorus atom.

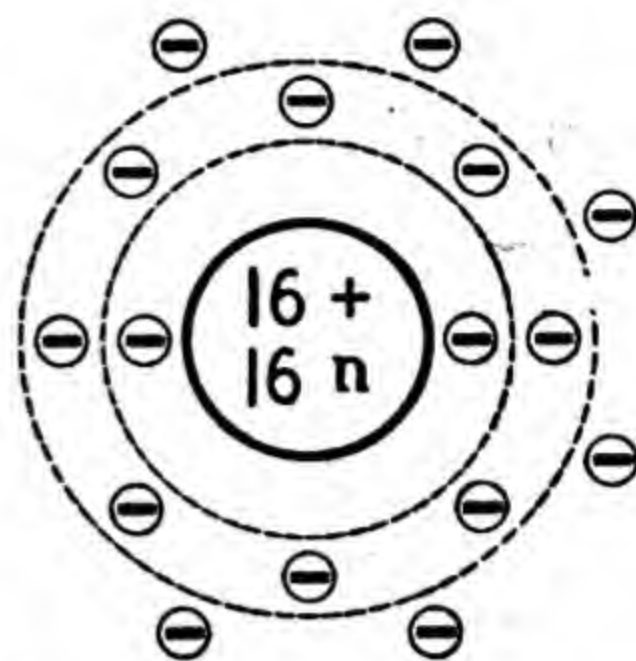


Fig. 80. The sulfur atom.

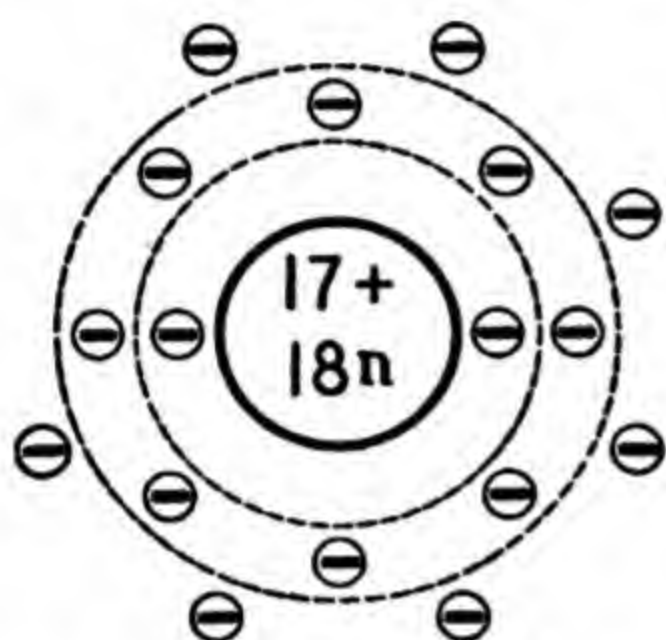


Fig. 81. The chlorine atom.

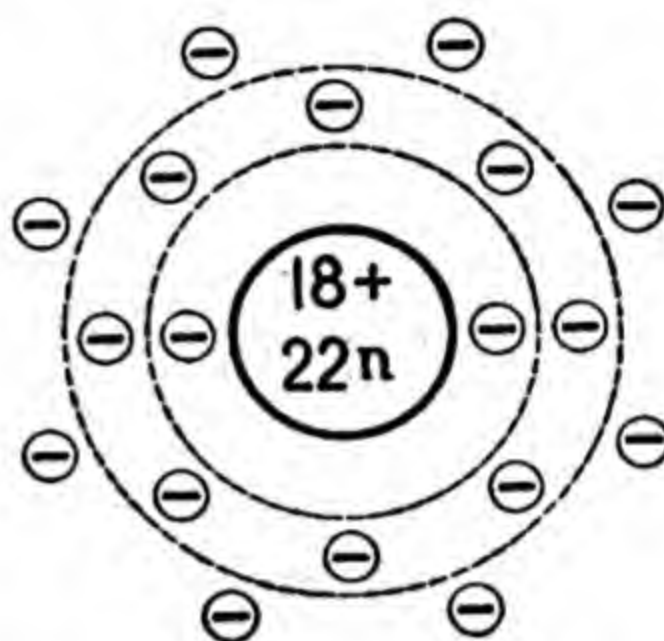


Fig. 82. The argon atom.

The structures of the higher atoms are considered in Part 4, pages 134 and 135.

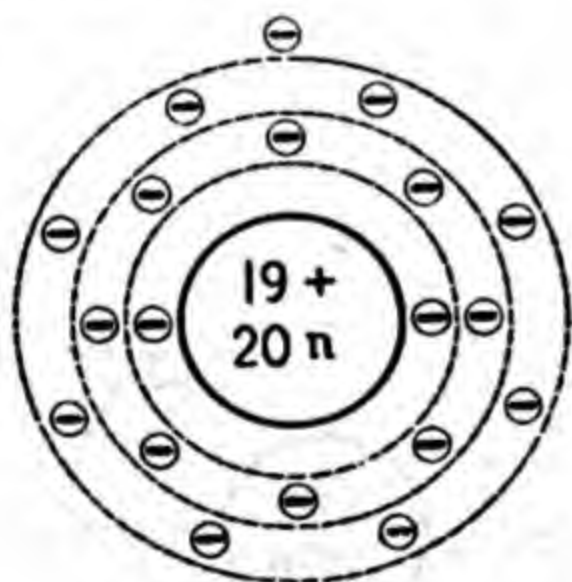


Fig. 83. The potassium atom. Nineteen protons and twenty neutrons in the nucleus. Nineteen electrons outside the nucleus. Atomic number, 19. Atomic weight, 39.

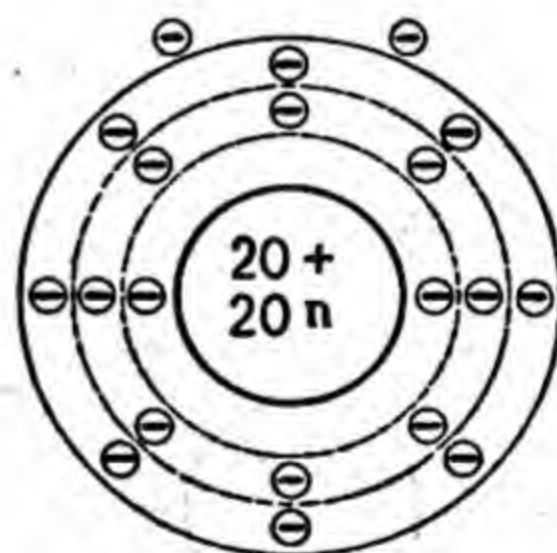


Fig. 84. The calcium atom. Twenty protons and twenty neutrons in the nucleus. Twenty electrons outside the nucleus. Atomic number, 20. Atomic weight, 40.

More concerning isotopes. We learned that not all hydrogen atoms have the same atomic weight. A few of them are twice as heavy and some three times as heavy as the ordinary hydrogen atom. How do the atoms of the heavy isotopes differ in structure from that of the light one?

All isotopes of an element have the same atomic number. The atomic number and not the atomic weight, therefore, deter-

mines the chemical properties of an element. Since the atomic number of deuterium is 1, it has one proton in the nucleus and one

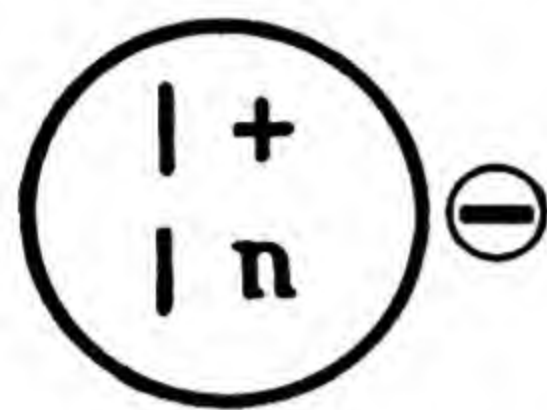


Fig. 85. The heavy hydrogen (deuterium) atom. One proton and one neutron in the nucleus. One electron outside the nucleus. Atomic number, 1. Atomic weight, 2. Often written ${}^2_1\text{H}$ to distinguish it from ordinary hydrogen ${}^1_1\text{H}$. The subscript before the symbol shows the atomic number of the element. The superscript before the symbol shows the atomic weight of the element.

electron in the first orbit, exactly like the light one. Its atomic weight, however, is 2, the nucleus consisting of one proton and one

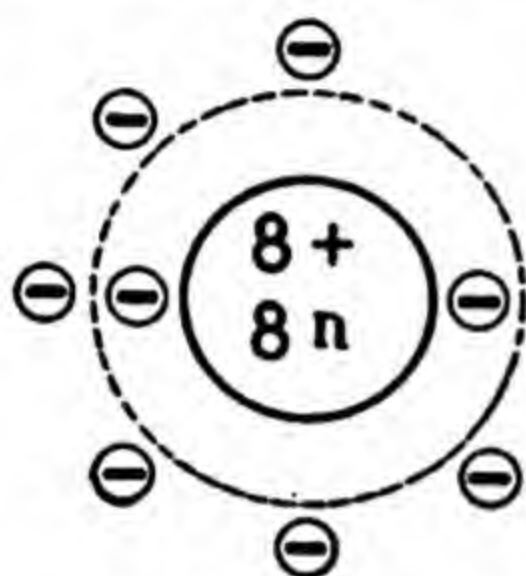


Fig. 86. The ordinary oxygen atom, ${}^{16}_8\text{O}$. Eight protons and eight neutrons in the nucleus. Eight electrons outside the nucleus. Atomic number, 8. Atomic weight, 16.

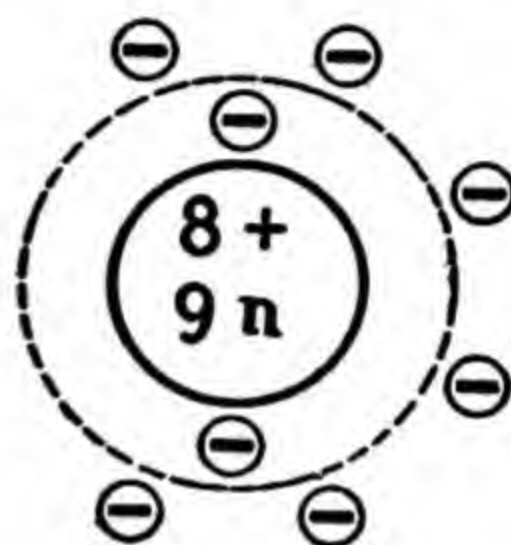


Fig. 87. A heavy oxygen atom, ${}^{17}_8\text{O}$. Eight protons and nine neutrons in the nucleus. Eight electrons outside the nucleus. Atomic number, 8. Atomic weight, 17.

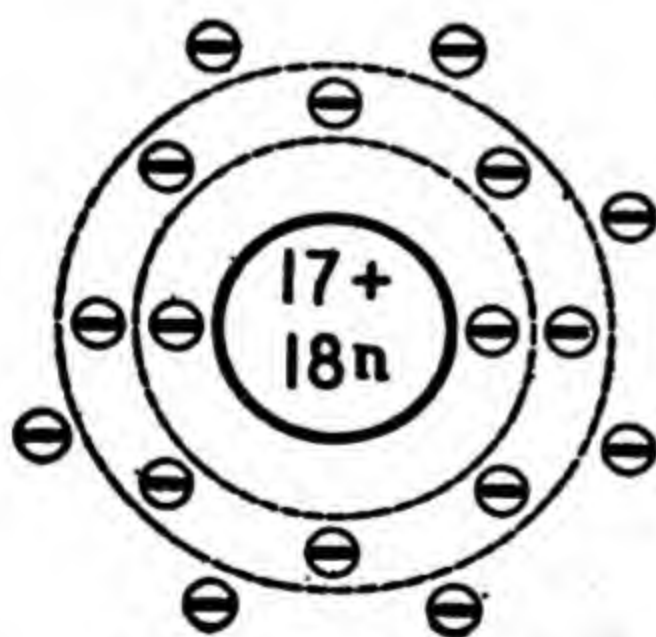


Fig. 88. The chlorine atom, ${}^{35}_{17}\text{Cl}$. Seventeen protons and eighteen neutrons in the nucleus. Seventeen electrons outside the nucleus. Atomic number, 17. Atomic weight, 35.

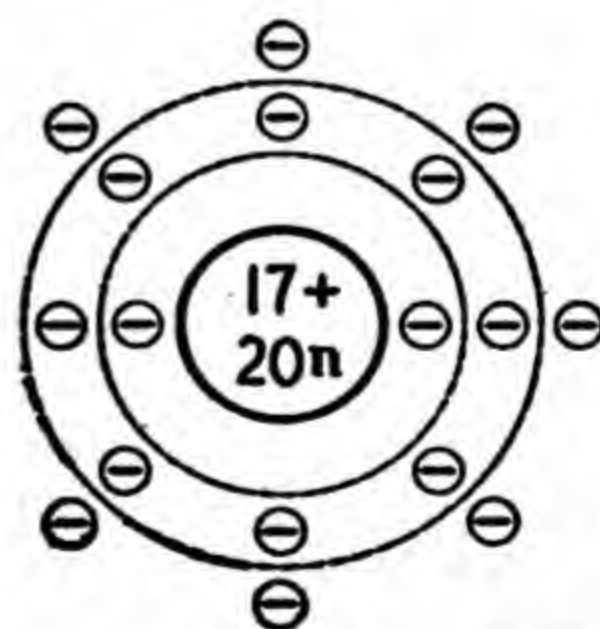


Fig. 89. The chlorine atom, ${}^{37}_{17}\text{Cl}$. Seventeen protons and twenty neutrons in the nucleus. Seventeen electrons outside the nucleus. Atomic number, 17. Atomic weight, 37.

neutron. Hydrogen of atomic weight 3 has one proton and two neutrons in the nucleus.

Three isotopes of oxygen have been discovered. The most common one has an atomic weight of 16, but there are oxygen atoms weighing 17 and 18 times as much as a hydrogen atom. They all have the atomic number 8, and hence are all atoms of the same element, oxygen.

The two isotopes of chlorine which have been discovered have atomic weights of 35 and 37.

Lithium, atomic weight 6, and boron, atomic weight 10, are shown in Figures 90 and 91.

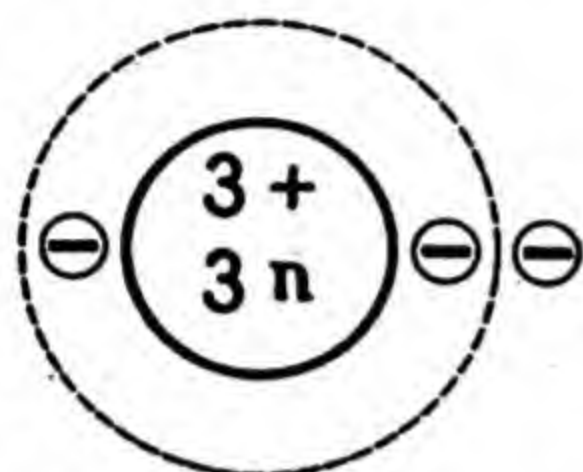


Fig. 90. The lithium atom, ${}^6_3\text{Li}$. Compare with ${}^7_3\text{Li}$, Fig. 67.

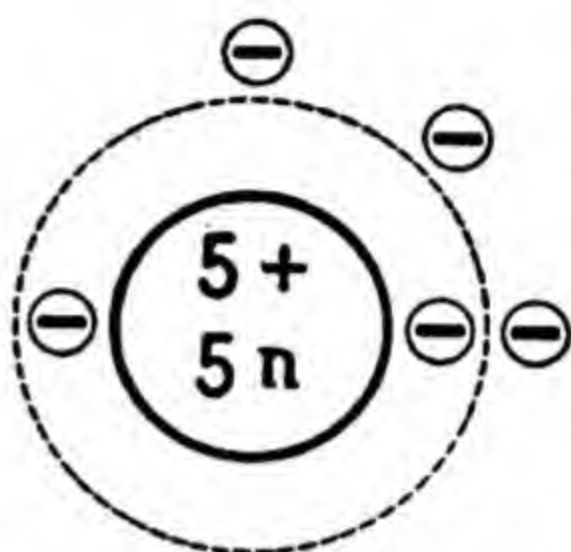


Fig. 91. The boron atom, ${}^{10}_5\text{B}$. Compare with ${}^{11}_5\text{B}$, Fig. 69.

Earlier, with some reservation, we defined an element as a substance composed of atoms which are all alike. We may now make a better definition: *An element is a substance composed exclusively of atoms which have the same atomic number.*

A list of some of the common elements for which isotopes have been discovered is shown below. The atomic weights of the isotopes are given, in each case, in the order of their abundance in nature.

			ISOTOPES			
H	1, 2		Si	28, 29, 30	Br	79, 81
He	4, 3		S	32, 36, 33, 34	Ag	107, 109
Li	7, 6		Cl	35, 37	Sn	120, 118, 116, 119, 117.
B	11, 10		A	40, 36, 38		124, 122, 112, 114, 115
C	12, 13		K	39, 41, 40	Ba	138, 137, 136, 135, 134,
N	14, 15		Ca	40, 44, 42, 48, 43, 46		130, 132
O	16, 18, 17		Fe	56, 54, 57, 58	Hg	202, 200, 190, 201, 198,
Ne	20, 22, 21		Cu	63, 65		204, 202
Mg	24, 25, 26		Zn	64, 66, 68, 67, 70	Pb	208, 206, 207, 204

Other isotopes of these elements have been produced in the cyclotron, but such isotopes are unstable. They undergo radioactive changes as described in Unit XXII, pages 504–510. The cyclotron is an electrical instrument in which protons and other very small electrically charged particles can be given high velocities and then be shot into ordinary matter. These extremely small particles, traveling at 10,000 miles per second, or faster, can

penetrate the nuclei of atoms and cause changes which are not duplicated by ordinary chemical reactions.

Questions and Exercises

1. State two views that have been held with reference to the nature of matter.
2. Define the following words: (a) proton, (b) electron, (c) neutron, (d) nucleus, (e) electron orbit.
3. If common substances contain protons and electrons, why are they electrically neutral?
4. How many electrons and how many protons are there in an ordinary hydrogen atom?
5. How many electrons, neutrons, and protons are there in a deuterium atom (hydrogen of atomic weight 2)?
6. Draw a picture showing how the electrons, neutrons, and protons are assembled in the oxygen atom.
7. Magnesium has an atomic number of 12 and an atomic weight of 24. Draw a schematic picture of the magnesium atom, indicating the number of electrons in each of the electron orbits.
8. The atomic number of sulfur is 16. Its atomic weight is 32. Draw a picture of the sulfur atom.
9. What are isotopes?
10. Account for the fact that the isotopes of any one element have different atomic weights but have the same atomic number.
11. Is the nucleus of an atom electrically charged or is it neutral?
12. Is the atom as a whole electrically charged or neutral? Explain.
13. Neon has three isotopes with masses 20, 21, and 22. The atomic number of neon is 10. How many protons and how many neutrons are there in the nucleus of each isotope?
14. What are some of the results of the discovery of the radioactive substances?
15. Where is the main part of the weight of an atom located?
16. What determines the atomic number of an atom? What determines its atomic weight?
17. Make drawings of the atoms of the first 20 elements, showing the probable arrangements of the protons and neutrons in the nucleus of each atom and of the electrons outside the nucleus.
18. Draw pictures of the isotopes of lithium. Its atomic number is 3; its atomic weights are 6 and 7.

PART 3

The Periodic Table

The Formation of Compounds from Elements

Early classification of the elements. For more than a century chemists have known that the elements fall naturally into groups or families, because of similarities in chemical properties, but no attempt was made to classify them until after the middle of the nineteenth century. In 1863 Newland, an English scientist, pointed out that if the elements are arranged in the order of their atomic weights, they fall into groups of eight, similar properties recurring in each octet. Other scientists, however, paid little attention to Newland's "octet theory."

The Periodic Table. Mendelejeff, a Russian chemist, revived Newland's idea in 1869. He presented the case so clearly and enthusiastically that chemists everywhere accepted his so-called "Periodic System," and they have made use of it ever since. It has been a valuable aid in a study of the elements. Instead of memorizing a description of every one of the 92 elements, we study in detail one or two elements in each group, or family, and from their properties we can estimate quite well the properties of other elements in the same group.

Instead of using atomic weights as the basis for constructing the periodic system, as Mendelejeff did, we now use the atomic numbers of the elements. This procedure is somewhat simpler and leads to similar results. In Mendelejeff's time the atomic numbers of the elements were not known. The first 12 elements in the order of their increasing atomic numbers are:

H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg
1	2	3	4	5	6	7	8	9	10	11	12

Lines connecting two elements in the above list indicate that the two elements are closely related. Helium and neon are alike in general properties, as are lithium and sodium. Beryllium and magnesium belong to the same family of elements. Let us now rearrange the elements, placing sodium under lithium, and magnesium under beryllium. We shall leave hydrogen and helium out of consideration for the present. Our table then assumes the following form:

Li	Be	B	C	N	O	F	Ne
3	4	5	6	7	8	9	10
Na	Mg						
11	12						

The element following magnesium is aluminum, Al, number 13. It falls logically into the position directly below boron, for its chemical properties are similar to those of boron. The next element, silicon, resembles carbon in many of its chemical properties; phosphorus and nitrogen form compounds of the same types; sulfur and oxygen are similar chemically; chlorine and fluorine resemble each other very closely. Argon, following chlorine in atomic number, falls under neon. Both are inert gases, and we have already learned of their similarity in properties (see page 36).

The next element, potassium, with an atomic number of 19, is placed under lithium and sodium, both of which it resembles very closely. Calcium falls logically under magnesium, scandium under aluminum. From there on, however, some of the elements differ considerably from those above them in the same columns. Mendelejeff recognized this discrepancy, and placed these elements to one side of the column, as members of subgroups. Titanium, vanadium, chromium, and manganese are the first representatives of the subgroups, IV', V', VI', and VII' respectively. (See Periodic Table, page 119.)

Obviously, iron, cobalt, and nickel are not inert gases, and therefore cannot be placed in column 8 under neon and argon. These three elements are placed aside, in so-called transition groups, A, B, and C. Then placing copper in subgroup I', zinc in II', etc., the row of eight is completed with krypton, which falls logically with the other inert gases in Column 8 or, in more customary notation, Group VIII. Rubidium, which is very similar in all of its properties to the other elements in column 1, falls under these, and strontium under calcium. This collection of eighteen elements (potassium through krypton) constitutes the first of the *long periods*. Each of the first two rows of eight elements is usually called a *short period*.

THE PERIODIC TABLE

I	I'	II	II'	III	III'	IV	IV'	V	V'	VI	VI'	VII	VII'	VIII	A	B	C
H 1		Be 4		B 5		C 6		N 7		O 8		F 9		He 2			
Li 3		Mg 12		Al 13		Si 14		P 15		S 16		Cl 17		Ne 10			
Na 11		Ca 20		Sc 21		Ti 22		V 23		Cr 24		Mn 25		A 18			
K 19														Kr 36		Co 27	Ni 28
	Cu 29						Ge 32		As 33		Se 34		Br 35				
Rb 37		Sr 38		Y 39		Zr 40		Cb 41		Mo 42				Xe 54		Rh 45	Pd 46
	Ag 47						Sn 50		Sb 51		Te 52		I 53				
Cs 55		Ba 56		La 57 See note													
						Hf 72		Ta 73		W 74		Re 75					
	Au 79					Pb 82			Bi 83		Po 84		— 85			Ir 77	Pt 78
		Ra 88		Ac 89		Th 90		Pa 91		U 92				Rn 86			
— 87																	

Following lanthanum, atomic number 57, there are twelve elements (atomic numbers 58 to 71, inclusive), which all belong in Group III. These are known as the *rare earth elements*. They are cerium, 58; praseodymium, 59; neodymium, 60; illinium, 61; samarium, 62; europium, 63; gadolinium, 64; terbium, 65; dysprosium, 66; holmium, 67; erbium, 68; thulium, 69; ytterbium, 70; lutecium, 71.

The next eighteen elements form a second long period. There are thirty-six elements in the next long period. The complete arrangement of all the elements is shown on page 119. A more modern table, showing to better advantage the location of the elements in the short and long periods, is shown on page 120. The solid lines join members of a main group, or family, of elements, while the dotted lines indicate that the elements constitute a subgroup.

The structure of an atom and its position in the Periodic Table. It is apparent that the explanation of this periodic repetition in the properties of the elements has something to do with the structure of the atom. What similarity exists in the structure of the lithium, sodium, and potassium atoms that gives them chemical properties which are almost identical? It can be seen from a study of the pictures of the lithium, sodium, and potassium atoms that the thing which they have in common is one electron in the outermost shell. Similarly, the beryllium, magnesium, and calcium atoms have two electrons in the outermost shell, boron and aluminum three, carbon and silicon four, nitrogen and phosphorus five, oxygen and sulfur six, fluorine and chlorine seven, neon and argon eight. This similarity in the number of electrons in the outermost shell holds true for other members of the same family; that is, for elements in the same group of the Periodic Table. It appears, therefore, that the chemical properties of an element are determined by the number of electrons in this shell. These electrons are called *valence* electrons, and the outermost shell is often called the *valence* shell.

Since hydrogen has one electron in its single orbit, it seems logical to place it directly above lithium in Group I. All members of this family have one electron in the outer orbit. The elements in Group VIII, the inert gases, all have eight electrons in the valence shell. This number of electrons is the greatest which the second shell ever holds. Since helium has two electrons in its single shell, and since two is the greatest number which the first shell in any element contains, helium is placed in Group VIII above the other elements, whose valence shells are completely filled.

Chemical reactions and atomic structure. We are now in a position to understand what actually happens when a chemical change takes place. It is assumed that a chemical reaction involves the giving up of electrons from the valence shell by one or more atoms and the acquiring of the electrons by another atom or atoms, or the reaction may involve a sharing of electrons by two or more atoms.

The elements with the valence shell completely filled are the most stable. All the elements in Group VIII of the Periodic Table are monatomic gases. No compounds involving any of these atoms have been found in nature. An atom which has a full valence shell cannot give up, acquire, or share electrons.

Formation of compounds from atoms of elements. Atoms have a tendency to make their outermost shells stable. This stabilizing can be done by acquiring electrons enough to bring the total number in the valence shell up to eight, or by losing all the electrons that are in a partially filled outer shell. For example, an atom in Group I of the Periodic Table might make its outer shell stable by giving one electron to some other atom or by acquiring seven electrons from other atoms. All the atoms with one valence

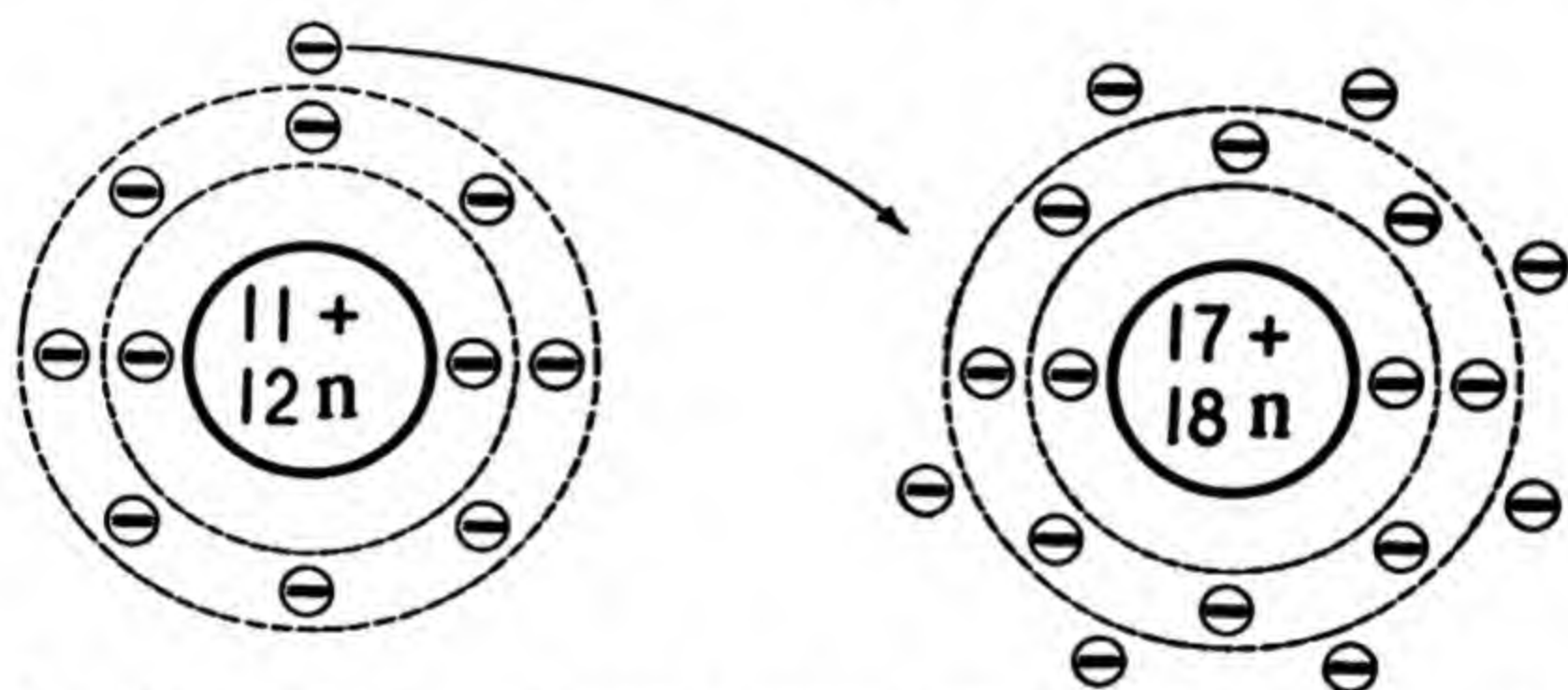


Fig. 92. A sodium atom yields one electron to a chlorine atom in forming sodium chloride.

electron prefer to give up their one electron in a chemical reaction. They do not capture seven electrons from other atoms.

The hydrogen atom often acquires a second electron, as, for instance when it combines with an element in Group I to form a hydride. The atom then has the electron structure of helium, and the valence shell contains the maximum number of electrons which it can hold.

Let us see what takes place when sodium reacts with chlorine gas. Each atom of chlorine has seven valence electrons, and requires one more to round out its valence shell. Since sodium has a tendency to give up its valence electron readily, each sodium atom gives one electron to each chlorine atom. Before the sodium atom gives up its electron, it is electrically neutral. After it has lost its valence electron, it is positively charged, since it still has eleven excess protons in the nucleus and now only ten electrons outside the nucleus.

Before receiving the electron from the sodium atom, the chlorine atom was neutral, having a positive charge of 17 in its

nucleus, and 17 electrons outside the nucleus. After the reaction, there are still 17 positive charges in the nucleus, but 18 electrons outside the nucleus. The atom is then charged negatively. Since opposite electrical charges attract each other, the positive sodium atoms are held close to the negative chlorine atom. In the gaseous state, they unite in pairs, forming molecules. In the solid state, a lattice of alternating positively charged sodium atoms and negatively charged chlorine atoms is formed. (See Fig. 19.) Compounds like sodium chloride, which are formed by an interchange of electrons, are called *ionic*, and the separate electrically charged atoms are called *ions*. These ions are said to possess *electrovalence*.

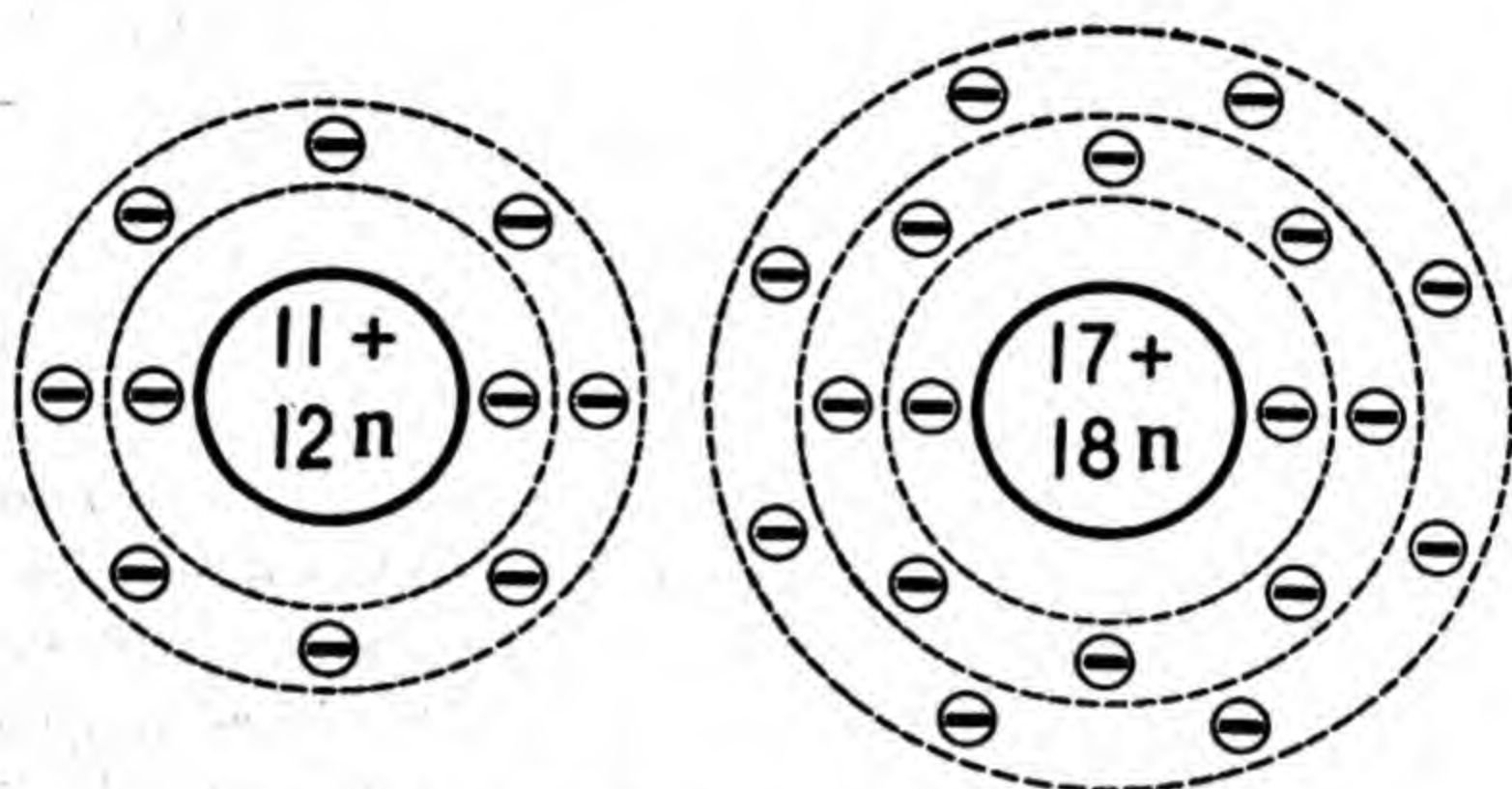


Fig. 93. The sodium chloride molecule.

If we allow the symbol of an element to stand for a single atom of the element, we may represent the composition of sodium chloride by NaCl . This is the *formula* of sodium chloride. It tells us that when sodium and chlorine react to form sodium chloride, the atoms of these elements combine in the ratio of one to one. The formula of a compound tells us the kinds of atoms and the number of each kind in a molecule of the compound.

What happens when an element with two valence electrons, like magnesium, reacts with one having seven electrons, like fluorine? Since each fluorine atom can acquire only one electron, and a magnesium atom gives up two, one atom of magnesium must react with two atoms of fluorine, as shown in Fig. 94. It is customary to write first in the formula the atom which loses electrons.

When an atom like magnesium, having two valence electrons, reacts with one like oxygen, which requires two electrons to fill its valence orbit, a compound will be formed by the union of one of each of these atoms. Magnesium oxide, for example, has the formula MgO .

When an atom with three valence electrons, like aluminum, reacts with one requiring two electrons, like oxygen, it can be seen that the fewest atoms which can react in this manner are five—two aluminum atoms together giving up six electrons, and three oxygen atoms together acquiring six electrons. The molecule of aluminum oxide therefore has the formula Al_2O_3 .

We know that hydrogen and oxygen react to form water. Let us see what changes take place in the atoms involved during

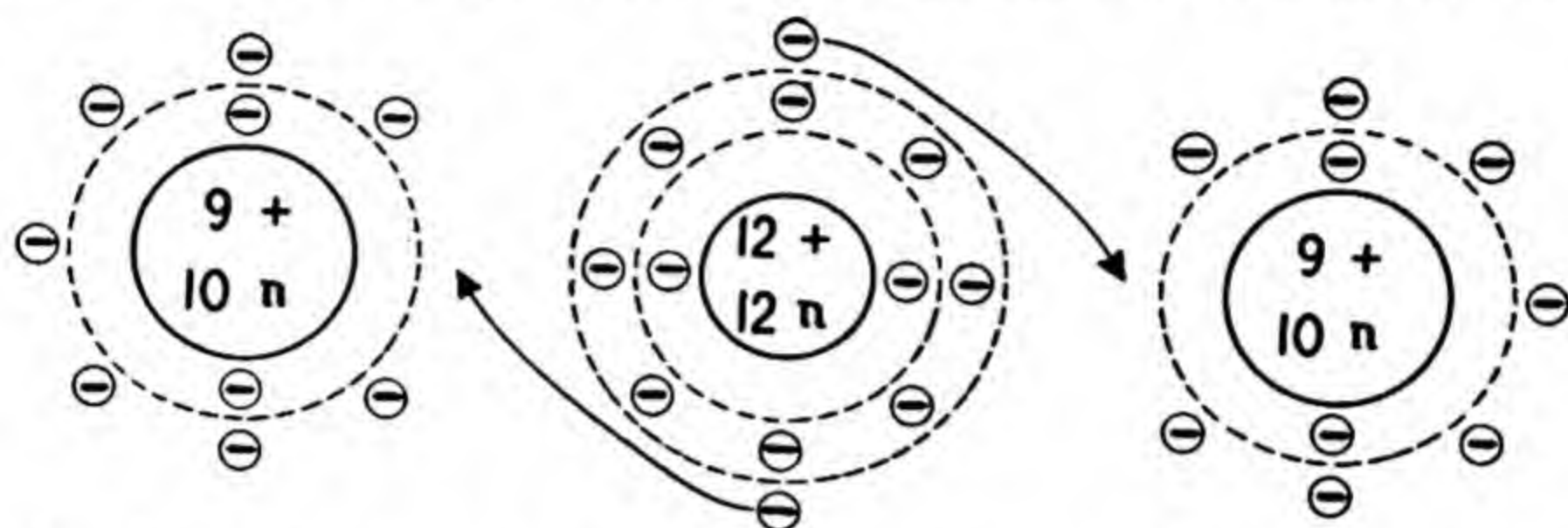


Fig. 94. Magnesium delivers an electron to each of two fluorine atoms in forming magnesium fluoride, MgF_2 .

the reaction. An oxygen atom has six valence electrons. It can assume a stable structure in its outer shell either by acquiring two electrons or by losing six. We might expect an oxygen atom to acquire an electron from each of two hydrogen atoms, but a hydrogen atom does not release its electron entirely to oxygen. It has a tendency to complete its own outer shell. A completed outer shell of a hydrogen atom contains two electrons (helium structure). One atom of oxygen, therefore, shares a pair of

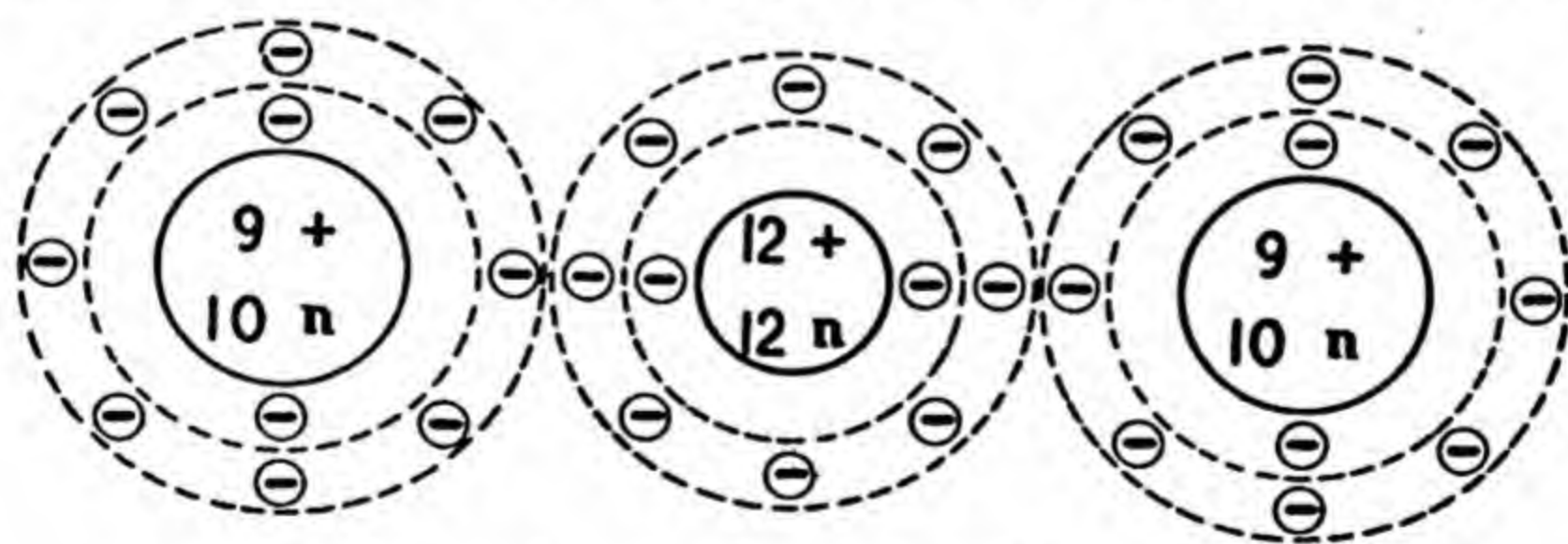


Fig. 95. The magnesium fluoride molecule.

electrons with each of two hydrogen atoms, the result being a partial ownership of electrons by each of the atoms involved in the union. The oxygen atom, however, has a stronger affinity for the electrons than have the hydrogen atoms, so that the shared electrons are held closer to the oxygen atom than they are to the hydrogen atoms. Hence the oxygen atom is, on the whole, more negative than the hydrogen atoms and the water molecule is *polar*, although there is no complete transfer of electrons. The

formation of a molecule of water may be represented by Figures 96 and 97.

The elements in Group IV of the Periodic Table have four valence electrons. The outer orbit may become stable by either

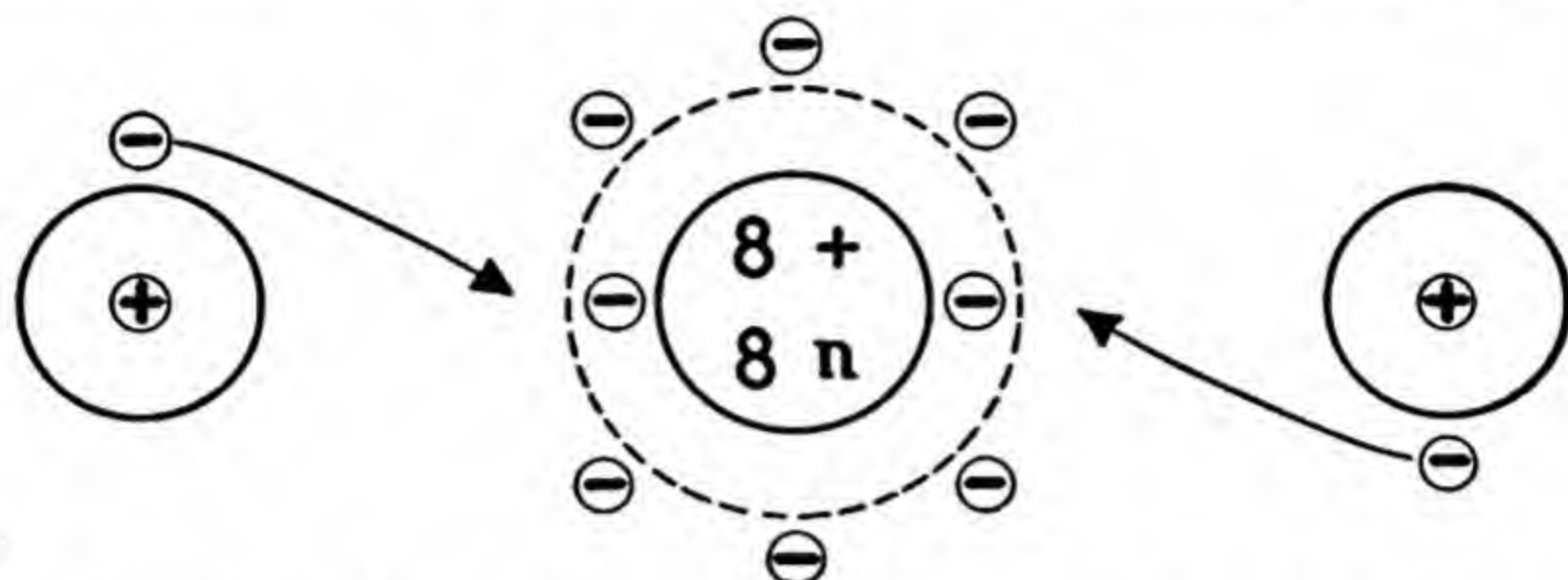


Fig. 96. An oxygen atom acquires an electron from each of two hydrogen atoms in forming a molecule of water. These electrons, however, do not become the exclusive property of the oxygen atom. Each hydrogen atom shares a pair of electrons with the oxygen atom. Water is only slightly ionized.

the loss or the gain of four electrons. When carbon and chlorine or carbon and hydrogen react, we have an example of shared electrons. The carbon does not give up an electron entirely to the chlorine as lithium does, but shares it with the chlorine atom. Likewise carbon and hydrogen atoms share electrons. In this

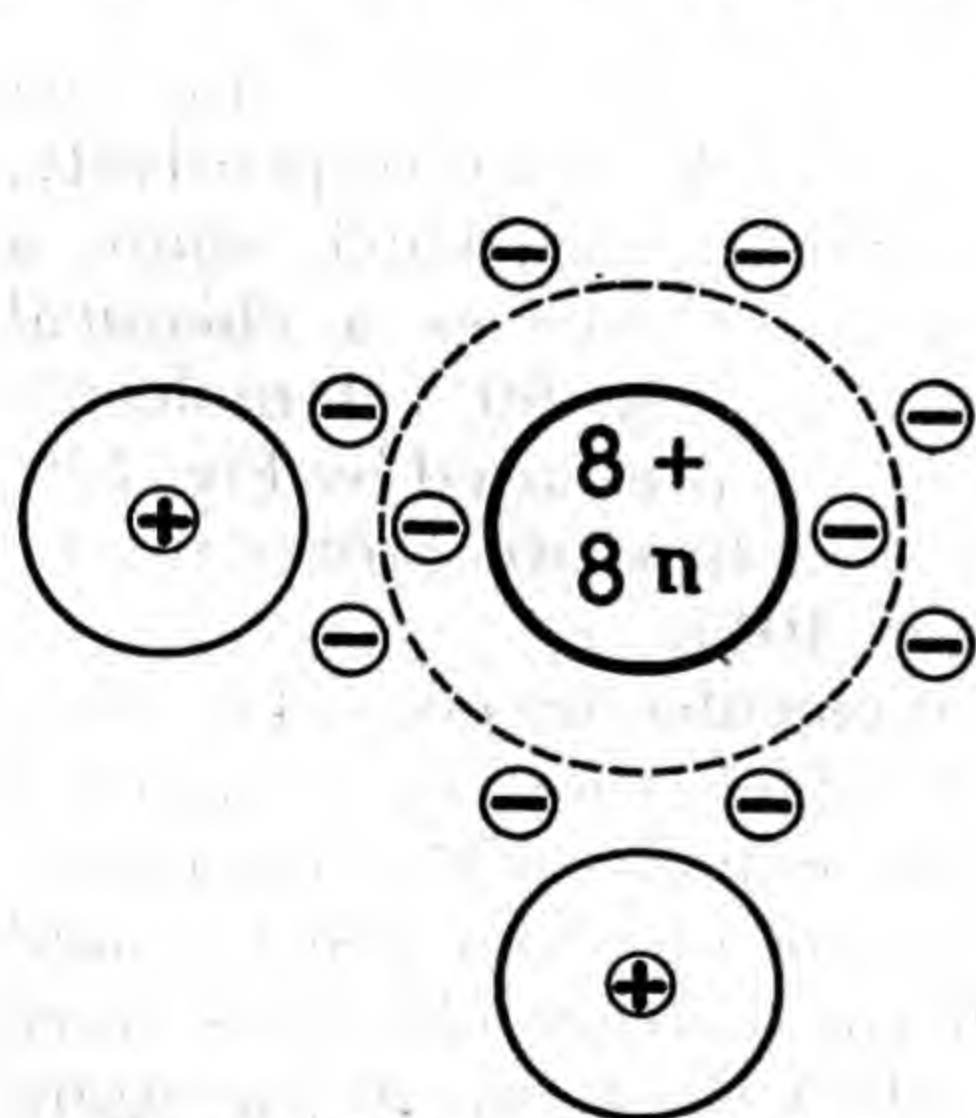


Fig. 97. The water molecule.

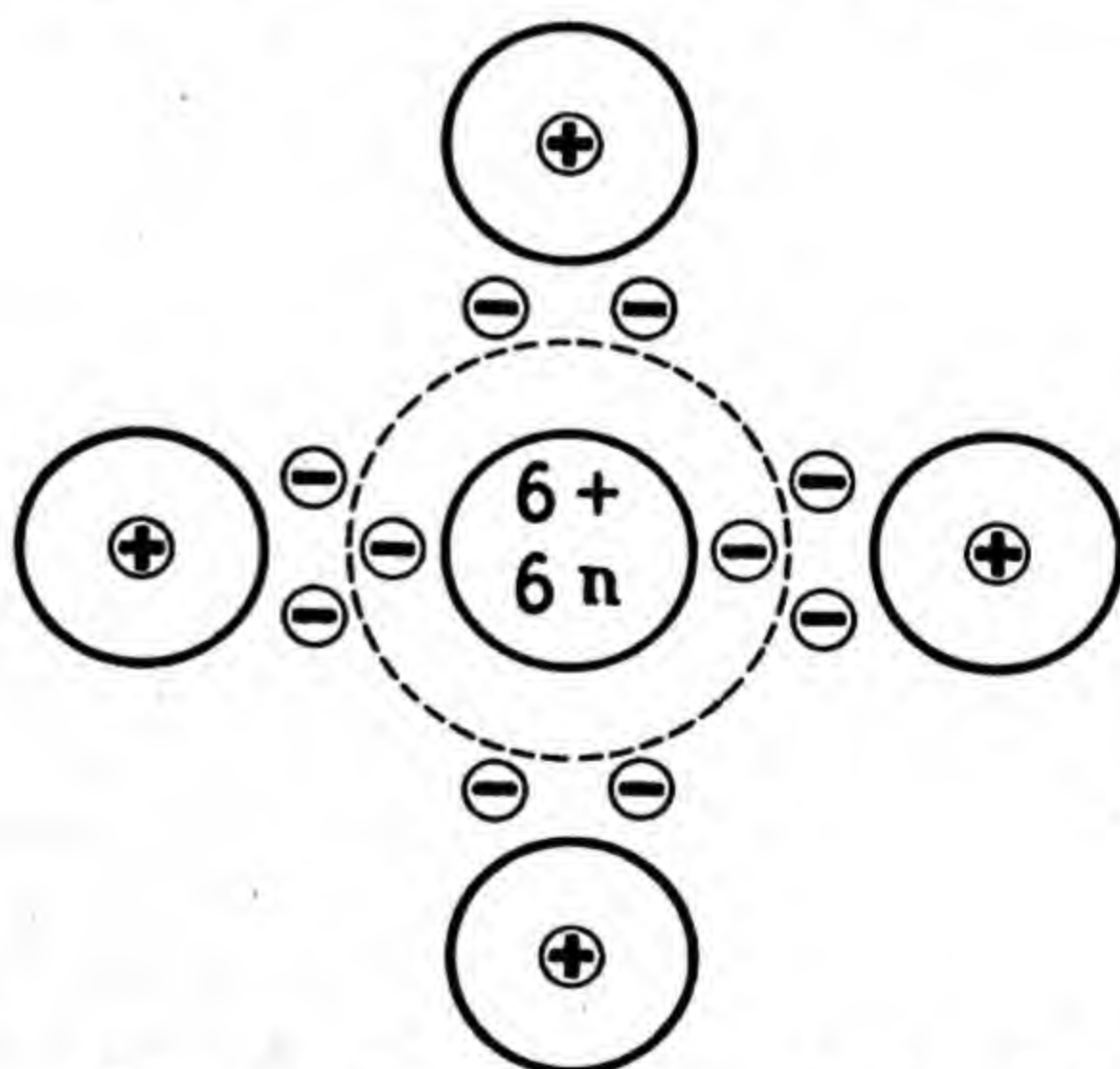


Fig. 98. The methane molecule. Each hydrogen atom shares two electrons with the carbon atom.

way all the atoms concerned have the valence orbits in a stable condition. A pair of electrons forms a chemical bond which holds two atoms together. The atoms making such a molecule are said to possess *covalence*, and if the electrons are shared equally

by the atoms involved, the compound is *nonpolar*. In some cases, both electrons which make up the chemical bond are supplied by one of the atoms. The ammonium radical is an example of this sort of linkage.

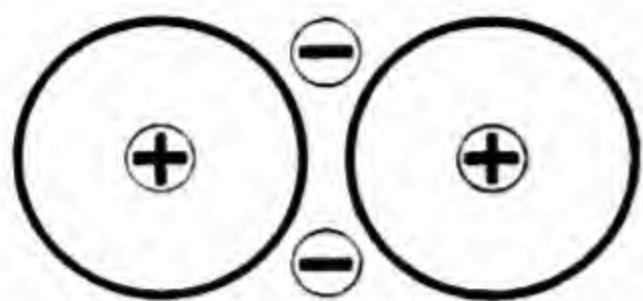


Fig. 99. The hydrogen molecule. A pair of electrons is shared by two hydrogen atoms.

Molecules of the common gaseous elements. In the so-called inert gases, which have only one atom in the molecule, the formula for the molecule is the same as the symbol for the atom. The

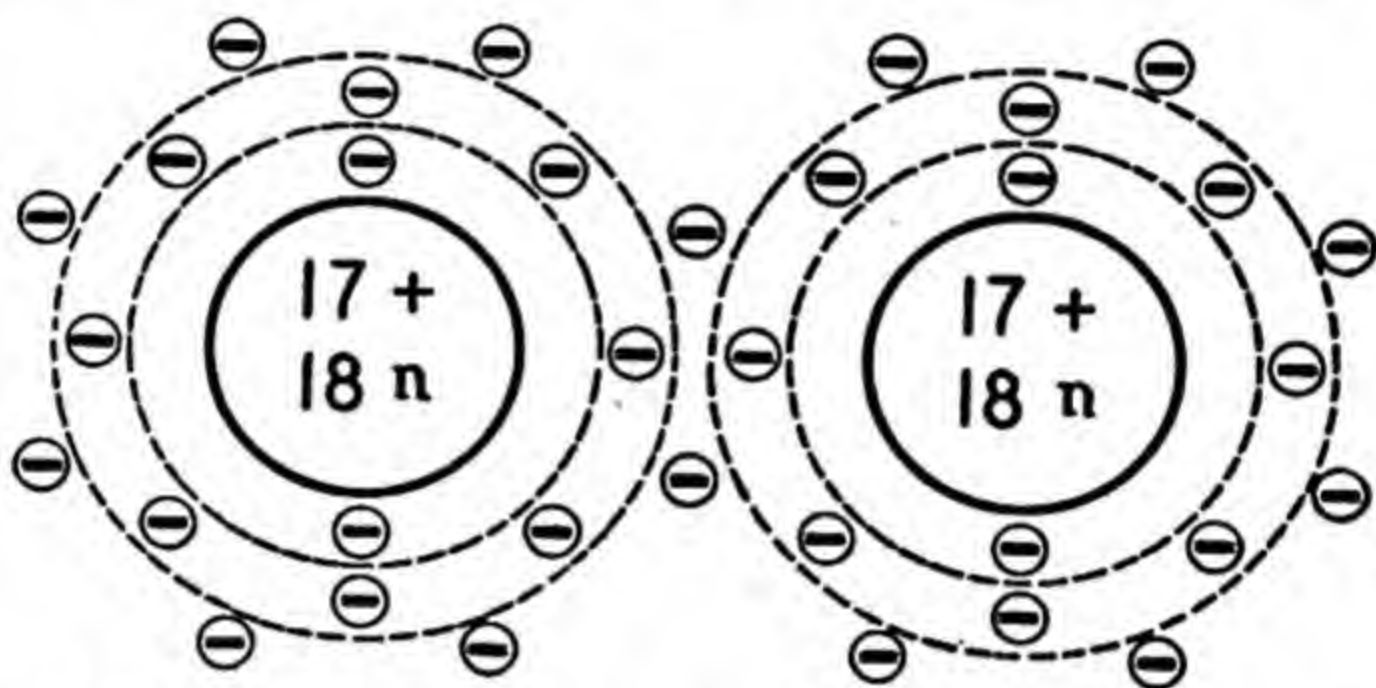


Fig. 100. The chlorine molecule. Formula, Cl_2 .

symbols He, Ne, Ar, Kr, and Xe stand for one atom or for one molecule of helium, neon, argon, krypton, and xenon, respectively.

The hydrogen molecule contains two atoms, which share a pair of electrons. This pair of electrons serves as a chemical bond between the two atoms, as shown in Fig. 99. A molecule of chlorine gas is represented by Fig. 100. Fluorine gas also has two atoms in the molecules (Fig. 101).

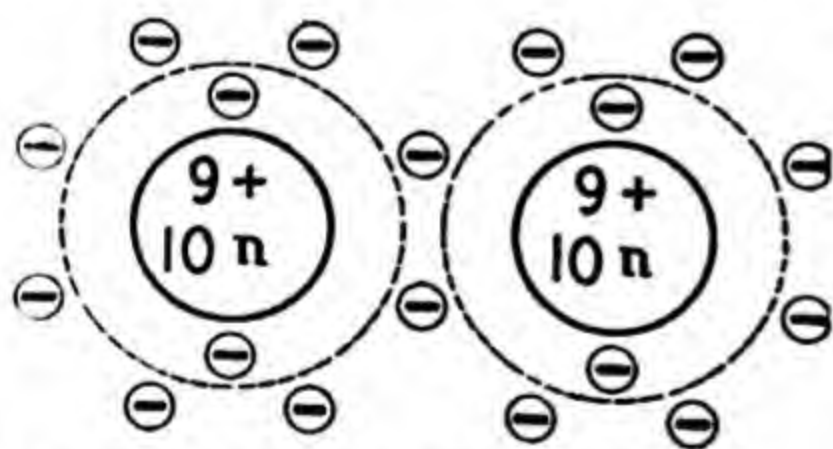


Fig. 101. The fluorine molecule. Formula, F_2 .

All these molecules are nonpolar, since the atoms of which they are composed share electrons equally with each other.

The portion of an atom which would remain if all the valence electrons were removed is called the *kernel* of the atom.

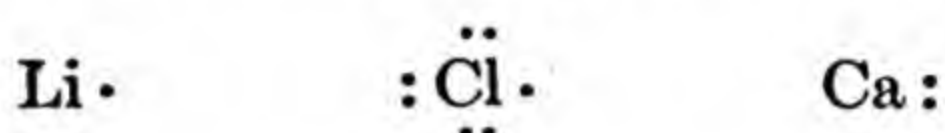
Since the valence electrons of an element are the only electrons immediately concerned in chemical changes, it is often convenient to represent the entire atomic structure underlying the valence shell (that is, the kernel) by the symbol of the element and the valence electrons by dots associated with this symbol.

In the following scheme the valence shells and the kernels of some elements are segregated. Numbers in ordinary type

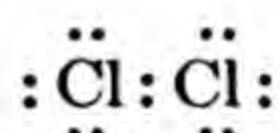
Atom	Nuclear Charge	Electrons			
		1st shell	2nd shell	3rd shell	4th shell
Li	+3	2	1		
Cl	+17	2	8	7	
Ca	+20	2	8	8	2

represent kernels of the atoms. Valence electrons are shown in heavy type.

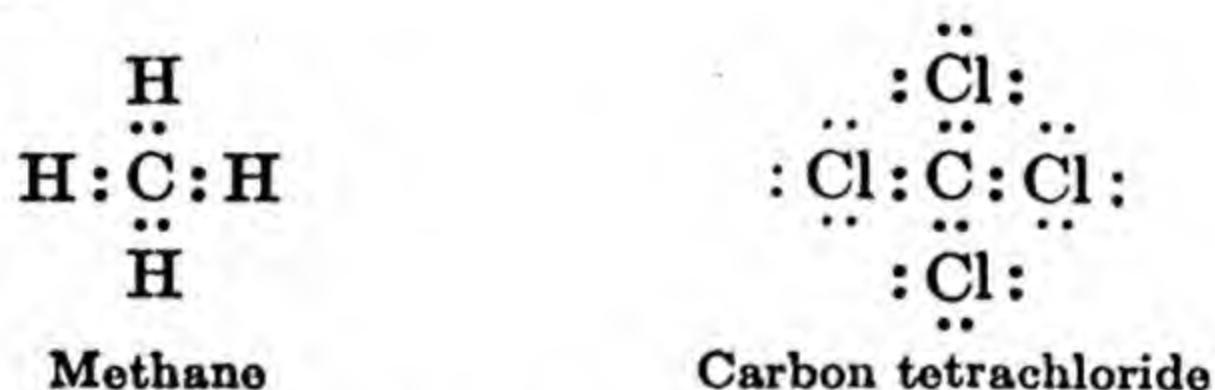
The atoms in the table may be pictured as follows:



Using the same scheme, the chlorine molecule would be represented by



and the formulas for methane and carbon tetrachloride may be written as follows:



Valence. From the formulas which we have just written it is clear that the atoms of the various elements do not all have the same combining capacity. One atom of magnesium combines with one atom of oxygen, forming MgO , while two atoms of hydrogen combine with one atom of oxygen, forming H_2O . The combining capacity of a magnesium atom is twice as great as the combining capacity of a hydrogen atom. The chemical name for combining capacity is *valence*.

It is easy to understand this difference in the combining capacity of different elements if we think of the structures of the atoms involved. Oxygen has six valence electrons, and thus needs two more in order to complete its outer shell of eight electrons. Since magnesium has two valence electrons, obviously one atom of magnesium can just supply the oxygen atom with these two needed electrons. Since each hydrogen atom has only one valence

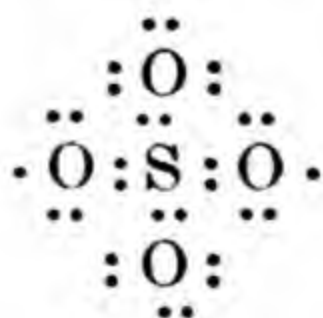
electron, two hydrogen atoms are required to supply the two electrons to a single oxygen atom.

The valence of hydrogen is one, since one valence electron is involved when it enters into chemical reactions. Lithium, sodium, potassium, and the other elements of Group I of the Periodic Table also have a valence of one, since each of these elements possesses one valence electron. Similarly, calcium, barium, and strontium are said to have a valence of two, aluminum of three and carbon of four.

Radicals. In some compounds we find a group of atoms that stay together through many chemical reactions and act like a single atom. Such a group of atoms is called a *radical*. Sulfuric acid, H_2SO_4 , contains the sulfate radical SO_4 . Since two atoms of hydrogen combine with one sulfate radical, this radical, SO_4 , is said to have a valence or combining capacity of 2. Nitric acid, HNO_3 , contains the nitrate radical NO_3 . This group of four atoms acts as a unit in many chemical reactions. Since it combines with one hydrogen atom in nitric acid, the radical NO_3 has a valence of 1.

The hydroxides, such as LiOH , NaOH , and KOH , contain the OH radical, which has a valence of 1. Ammonium hydroxide, NH_4OH , contains both the NH_4 and OH radicals. Since the OH radical has a valence of 1 and it combines with one NH_4 group, the valence of the NH_4 radical also is 1. Some other common radicals are bicarbonate, HCO_3 , with a valence of 1; carbonate, CO_3 , with a valence of 2; and phosphate, PO_4 , with a valence of 3.

Compounds containing radicals often contain covalent as well as electrovalent linkages. A compound like sodium sulfate, Na_2SO_4 , illustrates this situation. The sulfur atom is thought to share electrons with the oxygen atoms, the atoms being held together by covalent linkages.



Since sulfur and oxygen atoms contain only six valence electrons per atom, two more electrons are required to complete the outer orbit of each of two oxygen atoms. An element like sodium, which readily gives up electrons, can supply these needed electrons, each of two sodium atoms supplying one electron. The sulfate radical, after receiving the two electrons, contains a double negative charge, and the sodium ions (the atoms minus their valence

electrons), being positively charged, are bound to the sulfate ion (negatively charged radical) by electrovalence.

Formulas of compounds containing radicals. When magnesium, with a valence of 2, combines with the radical NO_3 , with a valence of 1, the formula is written $\text{Mg}(\text{NO}_3)_2$. The nitrate radical is enclosed in parentheses to show that there are two such radicals combined with the single magnesium atom. Likewise the formula for magnesium hydroxide is written $\text{Mg}(\text{OH})_2$, for if it were written MgOH_2 , the formula would say that the compound contains only one oxygen atom, which is incorrect. Magnesium sulfate is written MgSO_4 , since Mg and SO_4 each has a valence of 2. When the phosphate radical PO_4 , which has a valence of 3, reacts with magnesium, the formula for the product, magnesium phosphate, must be written $\text{Mg}_3(\text{PO}_4)_2$. We arrive at the same result if we consider the exchange of electrons involved in the reaction. The phosphate radical is capable of receiving three electrons (valence 3). The magnesium atom can yield two electrons (valence 2). Three magnesium atoms, each giving two electrons, a total of six, are required to satisfy two phosphate radicals, each taking three electrons, again a total of six; and the formula becomes $\text{Mg}_3(\text{PO}_4)_2$.

As explained on page 127, the valence of an atom corresponds to the number of electrons it yields, or receives, or the number of pairs of electrons it shares in forming a compound. Atoms which lose electrons form positive ions and atoms which acquire electrons form negative ions. The valences of such atoms correspond to the number of electrical charges held by the corresponding ions.

VALENCES OF SOME COMMON ATOMS AND RADICALS

Valence 1	Valence 2	Valence 3	Valence 1	Valence 2	Valence 3
H^+ Li^+ Na^+ K^+ NH_4^+ Ag^+ $^*\text{Hg}^+$	Cu^{++} Ca^{++} Ba^{++} Pb^{++} Zn^{++} $^*\text{Fe}^{++}$ $^*\text{Hg}^{++}$	$^*\text{Fe}^{+++}$ Al^{+++}	F^- Cl^- Br^- OH^- NO_3^- HCO_3^-	O^{--} S^{--} SO_4^{--} CO_3^{--}	PO_4^{---}

*Some elements have more than one valence.

Questions and Exercises

1. What similarity in atomic structure is there in the elements that constitute a vertical group in the Periodic Table?

2. What differences in atomic structure exist between members of a single group in the Periodic Table?

3. Magnesium has properties similar to those of beryllium, calcium, and radium. Can you find any way to account for this fact?

4. Is the Periodic Table based upon a theory or is it based upon experimental evidence?

5. Why are the gases in Group VIII of the Periodic Table called "inert gases"?

6. Show by drawings of the atoms what takes place when: (a) magnesium reacts with sulfur, forming magnesium sulfide; (b) boron reacts with oxygen, forming boron oxide; (c) calcium reacts with chlorine, forming calcium chloride; (d) potassium reacts with nitrogen, forming potassium nitride; (e) silicon reacts with oxygen, forming silicon dioxide.

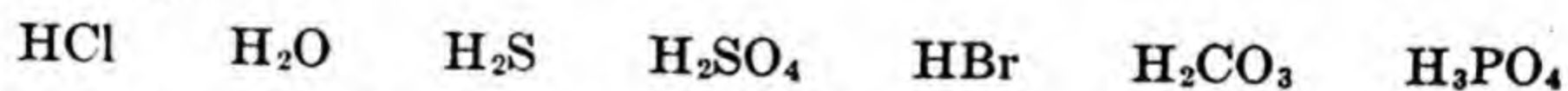
7. Write the formula for each of the compounds formed in Exercise 6.

8. Fill in the formulas of the compounds formed when the ions at the left react with those at the top of the table on page 131. Write the formulas on the dotted lines.

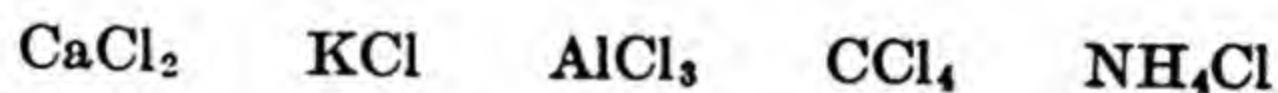
9. What information is conveyed to you by the following formulas: (a) $C_{12}H_{22}O_{11}$, sugar; (b) H_2SO_4 , sulfuric acid; (c) HNO_3 , nitric acid; (d) H_3PO_4 , phosphoric acid?

10. When sulfur burns, one molecule of oxygen combines with one atom of sulfur to form one molecule of sulfur dioxide. Show by drawings of the atoms what takes place during the reaction. Write the formula for sulfur dioxide.

11. State the valences of the atoms or radicals combined with hydrogen in the following compounds:



12. State the valences of the atoms or groups combined with chlorine in the following compounds:



13. What is the valence of barium in barium oxide, BaO ?

14. The molecule of acetic acid consists of two atoms of carbon, four of hydrogen, and two of oxygen. Write a formula for acetic acid.

15. Why are (a) four atoms of hydrogen needed for combination with one of carbon, (b) three atoms of hydrogen needed for combination with one of nitrogen, (c) five atoms of oxygen needed for combination with two of nitrogen? Assume that the oxygen receives electrons from the nitrogen.

Ions	F ⁻	Cl ⁻	Br ⁻	OH ⁻	NO ₃ ⁻	O ²⁻	S ²⁻	SO ₄ ²⁻	CO ₃ ²⁻	PO ₄ ³⁻
H ⁺										
Li ⁺										
Na ⁺										
K ⁺										
NH ₄ ⁺										
Ag ⁺										
Hg ⁺										
Cu ⁺⁺										
Ca ⁺⁺										
Ba ⁺⁺										
Pb ⁺⁺										
Zn ⁺⁺										
Fe ⁺⁺										
Hg ⁺⁺										
Fe ⁺⁺⁺										
Al ⁺⁺⁺										

PART 4

Structure of the Heavier Atoms

Each element in the second and third horizontal rows of the Periodic Table differs in structure from the one preceding it by one proton in the nucleus and one electron in a shell surrounding the nucleus. Each of these shells, with the exception of the first one, which never contains more than two electrons, is complete when it holds eight electrons.

There are, however, 18 elements in the fourth row of the Periodic Table, and the atomic structures of these are more complicated. Krypton, the inert gas in Group VIII, at the end of the fourth row, has the structure shown in the table below. Each element in this row has one more proton in the nucleus and one more electron outside the nucleus than has the element preceding it, but since there are 18 elements in the row, some of these electrons must enter the third shell while others are retained in the fourth. The third shell cannot hold more than 18 electrons.

Rubidium, the first element in the fifth row, has one more proton and one more electron than krypton, and this extra electron starts a new shell, as in the case of the members of Group I. Xenon, the last member of this row, has the structure indicated in the table below. Once again there are 18 elements in the row, and xenon has 18 electrons in the fourth shell, as well as a completed octet in the fifth.

The additional electron in the next element, cesium, starts a new orbit. This row contains 32 elements. Radon, the last

STRUCTURES OF THE INERT GASES

Element	Atomic number	Electrons in each shell
Helium.....	2	2
Neon.....	10	2, 8
Argon.....	18	2, 8, 8
Krypton.....	36	2, 8, 18, 8
Xenon.....	54	2, 8, 18, 18, 8
Radon.....	86	2, 8, 18, 32, 18, 8

element in this row, has the electronic structure indicated in the Table.

The rare earths. The elements with atomic numbers from 57 to 71 are all metallic in nature, and each has a valence of 3. They are collectively described as the rare-earth metals. Lanthanum, number 57, is similar to aluminum in its properties. Each of the succeeding elements, up to atomic number 71, instead of adding one electron to the valence shell, has an additional electron in an inner shell.

The table on pages 134–135 shows the arrangement of the electrons in the elements.

Exercise

1. Using as models the structures of the inert gases given in the table on pages 134–135, draw pictures of the atoms in (a) Group I of the Periodic Table; (b) Group VII of the Periodic Table; (c) Group II of the Periodic Table; (d) Group III of the Periodic Table.

ARRANGEMENT OF ELECTRONS IN VARIOUS ATOMS

Element	Atomic number	Number of electrons in various shells						
		1	2	3	4	5	6	7
H	1	1						
He	2	2						
Li	3	2	1					
Be	4	2	2					
B	5	2	3					
C	6	2	4					
N	7	2	5					
O	8	2	6					
F	9	2	7					
Ne	10	2	8					
Na	11	2	8	1				
Mg	12	2	8	2				
Al	13	2	8	3				
Si	14	2	8	4				
P	15	2	8	5				
S	16	2	8	6				
Cl	17	2	8	7				
A	18	2	8	8				
K	19	2	8	8	1			
Ca	20	2	8	8	2			
Sc	21	2	8	8	3			
Ti	22	2	8	8	4			
V	23	2	8	11	2			
Cr	24	2	8	13	1			
Mn	25	2	8	13	2			
Fe	26	2	8	14	2			
Co	27	2	8	15	2			
Ni	28	2	8	16	2			
Cu	29	2	8	18	1			
Zn	30	2	8	18	2			
Ga	31	2	8	18	3			
Ge	32	2	8	18	4			
As	33	2	8	18	5			
Se	34	2	8	18	6			
Br	35	2	8	18	7			
Kr	36	2	8	18	8			
Rb	37	2	8	18	8	1		
Sr	38	2	8	18	8	2		
Y	39	2	8	18	9	2		
Zr	40	2	8	18	10	2		
Cb	41	2	8	18	12	1		
Mo	42	2	8	18	13	1		
Ma	43	2	8	18	14	1		
Ru	44	2	8	18	15	1		
Rh	45	2	8	18	16	1		
Pd	46	2	8	18	18	—		

ARRANGEMENT OF ELECTRONS IN VARIOUS ATOMS.—(Continued)

Element	Atomic number	Number of electrons in various shells						
		1	2	3	4	5	6	7
Ag	47	2	8	18	18	1		
Cd	48	2	8	18	18	2		
Ln	49	2	8	18	18	3		
Sn	50	2	8	18	18	4		
Sb	51	2	8	18	18	5		
Ta	52	2	8	18	18	6		
I	53	2	8	18	18	7		
Xe	54	2	8	18	18	8		
Cs	55	2	8	18	18	8	1	
Ba	56	2	8	18	18	8	2	
La	57	2	8	18	18	9	2	
Ce	58	2	8	18	19	9	2	
Pr	59	2	8	18	20	9	2	
Nd	60	2	8	18	21	9	2	
Il	61	2	8	18	22	9	2	
Sm	62	2	8	18	23	9	2	
Eu	63	2	8	18	24	9	2	
Gd	64	2	8	18	25	9	2	
Tb	65	2	8	18	26	9	2	
Ds	66	2	8	18	27	9	2	
Ho	67	2	8	18	28	9	2	
Er	68	2	8	18	29	9	2	
Tm	69	2	8	18	30	9	2	
Yb	70	2	8	18	31	9	2	
Lu	71	2	8	18	32	9	2	
Hf	72	2	8	18	32	10	2	
Ta	73	2	8	18	32	11	2	
W	74	2	8	18	32	12	2	
Re	75	2	8	18	32	13	2	
Os	76	2	8	18	32	14	2	
Ir	77	2	8	18	32	15	2	
Pt	78	2	8	18	32	16	2	
Au	79	2	8	18	32	18	1	
Hg	80	2	8	18	32	18	2	
Tl	81	2	8	18	32	18	3	
Pb	82	2	8	18	32	18	4	
Bi	83	2	8	18	32	18	5	
Po	84	2	8	18	32	18	6	
—	85	2	8	18	32	18	7	
Rn	86	2	8	18	32	18	8	
—	87	2	8	18	32	18	8	1
Ra	88	2	8	18	32	18	8	2
Ac	89	2	8	18	32	18	9	2
Th	90	2	8	18	32	18	10	2
Pa	91	2	8	18	32	18	11	2
U	92	2	8	18	32	18	12	2

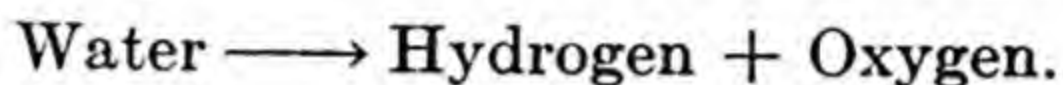
UNIT IV

Chemical Equations and Chemical Calculations

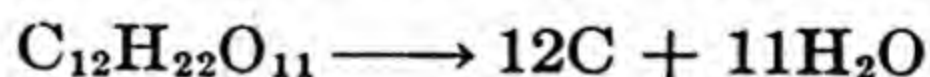
PART 1

Chemical Equations

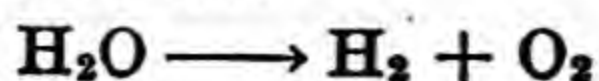
Writing chemical equations. For the chemical reactions which we have studied so far, we have written "word equations." On page 43 the decomposition of water was indicated as follows:



Such an equation tells us merely that water, when decomposed, yields hydrogen and oxygen. It tells us nothing about the composition of water itself, or how the molecules of oxygen and hydrogen are formed. The chemist writes reactions in a more enlightening manner. He uses the formulas instead of the names for the substances appearing in the reaction, including the substances that react, as well as the products that are formed. The formula of a substance tells us of what atoms that substance is composed and the number of each kind in a molecule of the substance. When the equation is properly balanced, we can follow the course of the reaction and can see exactly how the atoms change partners, or how some of them break away from others, forming new substances. The statement that sugar when heated gives off water, leaving carbon, means very little to a person who knows nothing about the composition of sugar. If, however, we write the formula for sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, and say that it breaks up into 12 carbon atoms and 11 molecules of water, it is not difficult to see what has taken place during the heating process. We may express this change in a chemical equation as follows:

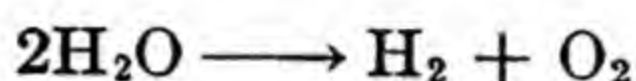


Balancing chemical equations. We know that the formula for water is H_2O , and that the formulas for hydrogen gas and oxygen gas are H_2 and O_2 , respectively. If these formulas are substituted for the names in the equation for the decomposition of water, the equation becomes:



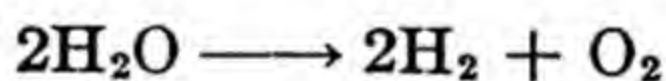
We can see at a glance that this equation is not "balanced." The formula O_2 shows that after the reaction is completed we have one molecule of oxygen consisting of two atoms of oxygen, although we started with one molecule of water containing only one atom of oxygen. Oxygen is not created in the process. Hence, we must show the source of the two atoms of oxygen.

If two molecules of water were decomposed, they would liberate two atoms of oxygen, which would combine to form one molecule of oxygen gas. We therefore place a 2 in front of the formula for water, indicating that two molecules of water are decomposed for every molecule of oxygen formed. Our equation then looks like this:



This accounts for the oxygen, but we see now that the number of hydrogen atoms on the two sides of the arrow is not the same. The two molecules of water together contain four atoms of hydrogen, and since one molecule of hydrogen gas consists of two hydrogen atoms, these four atoms must form two molecules of hydrogen gas.

If we place a 2 before the H_2 on the right side of the equation, indicating that two molecules of hydrogen are formed, our equation becomes:



This is a *balanced equation* for the decomposition of water into hydrogen and oxygen.

We shall now rewrite all the word equations which have been given in the preceding pages. These reactions may be placed in four main groups or kinds of chemical changes: (1) decomposition, (2) combination, (3) replacement, (4) double replacement or double decomposition. We shall write the reactions as they come under each of these headings.

Remember the following points in writing any chemical equation:

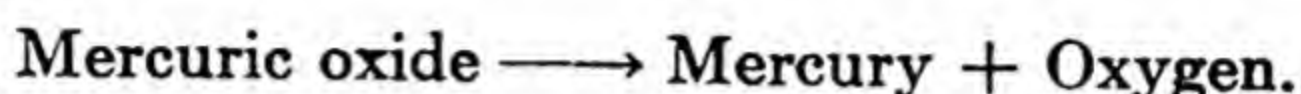
1. The correct formulas for the substances taking part in the reaction are written on the left side of the arrow.

2. The correct formulas for the substances formed by the reaction, the products of the reaction, are written on the right side of the arrow.

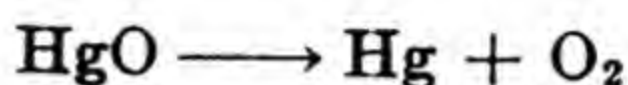
3. The equation must then be balanced; that is, correct numbers must be placed *in front* of the formulas so that the number of atoms of each element appearing in the equation is the same on both sides of the arrow.

Decompositions. The breaking up of water into hydrogen and oxygen is called a decomposition, because water breaks up into two simpler substances. Decomposition takes place also when mercuric oxide is heated. It breaks up to yield mercury and oxygen.

WORD EQUATION:

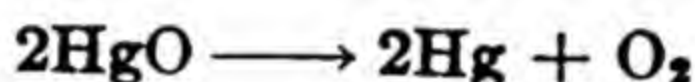


FORMULA EQUATION:



A molecule of a solid or liquid element is, for convenience, assumed to be a single atom. To balance the equation we must multiply HgO by two in order to show the source of the two atoms of oxygen in the molecule of oxygen gas. Then we must multiply the Hg by two, and the equation is balanced.

BALANCED EQUATION:

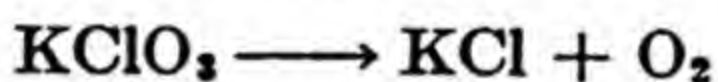


Heating potassium chlorate to obtain oxygen is also a typical decomposition reaction:

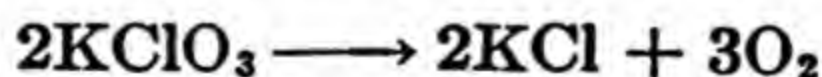
WORD EQUATION:



Writing formulas in place of words, we have the formula equation



This equation is balanced as follows:



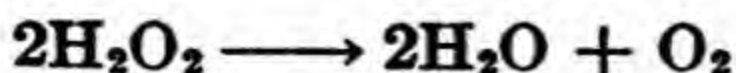
There is now the same number of atoms of each element on both sides of the equation.

The decomposition of hydrogen peroxide into water and oxygen gas is shown as follows:

WORD EQUATION:



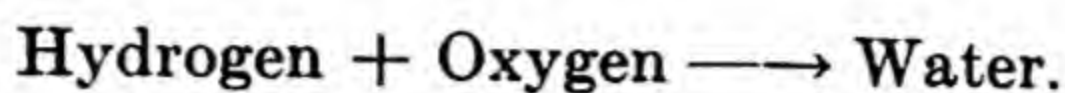
FORMULA EQUATION:



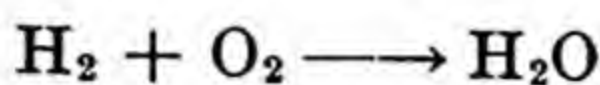
Combination. On page 44 we wrote word equations representing a form of chemical reaction called *combination*. In a

combination reaction two or more elements go together to form a compound. We shall rewrite those reactions, using formulas:

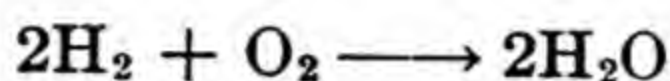
WORD EQUATION:



FORMULA EQUATION:



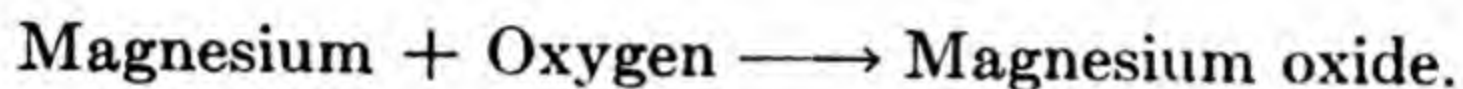
BALANCED EQUATION:



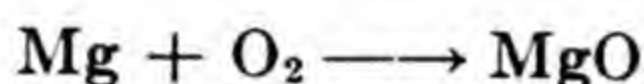
This equation is the reverse of the equation for the decomposition of water.

Similarly we may write the other reactions shown on page 44 as follows:

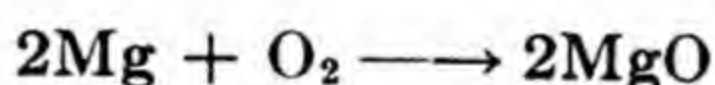
WORD EQUATION:



FORMULA EQUATION:



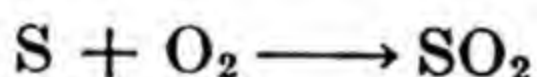
BALANCED EQUATION:



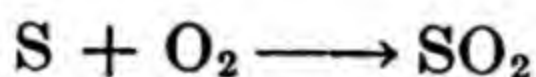
WORD EQUATION:



FORMULA EQUATION:



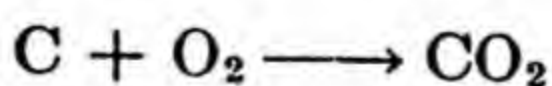
BALANCED EQUATION:



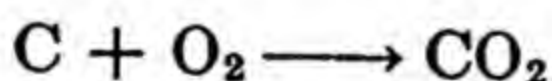
WORD EQUATION:



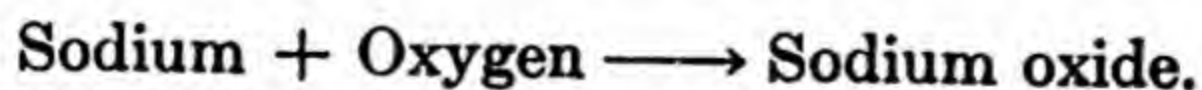
FORMULA EQUATION:



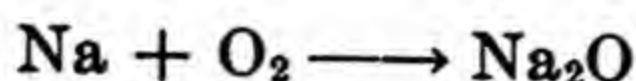
BALANCED EQUATION:



WORD EQUATION:



FORMULA EQUATION:



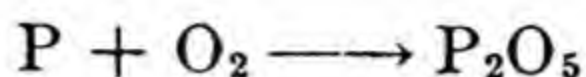
BALANCED EQUATION:



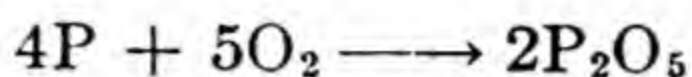
WORD EQUATION:

Phosphorus + Oxygen \longrightarrow Phosphorus pentoxide.

FORMULA EQUATION:



BALANCED EQUATION:



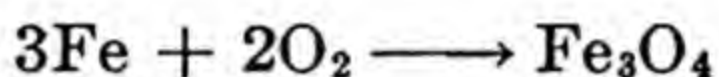
WORD EQUATION:

Iron + Oxygen \longrightarrow Magnetic iron oxide.

FORMULA EQUATION:



BALANCED EQUATION:



Replacement. The methods described for the preparation of hydrogen illustrate the type of reactions called *replacement*. In replacement, or simple replacement, as it is sometimes called, one element drives another out of a compound, forming a different compound with the element or radical which remains. The reaction between sodium and water is an example of this kind:

WORD EQUATION:

Sodium + Water \longrightarrow Hydrogen + Sodium hydroxide

FORMULA EQUATION:



BALANCED EQUATION:



Under ordinary conditions, a sodium atom drives out only one of the hydrogen atoms from the water molecule. The other hydrogen atom remains with the oxygen, but since a molecule of hydrogen gas has the formula H_2 , two sodium atoms must react and two water molecules must be decomposed every time one molecule of hydrogen is formed. We show this requirement in the equation by multiplying Na, HOH, and NaOH by two. The equation then balances.

The action of potassium on water is similar to that of sodium on water.

WORD EQUATION:

Potassium + Water \longrightarrow Hydrogen + Potassium hydroxide.

FORMULA EQUATION:

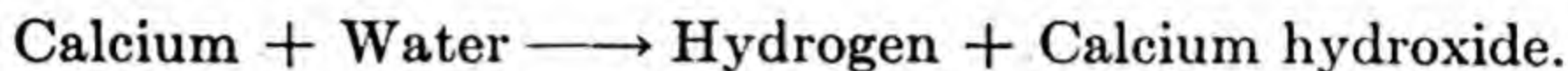


BALANCED EQUATION:

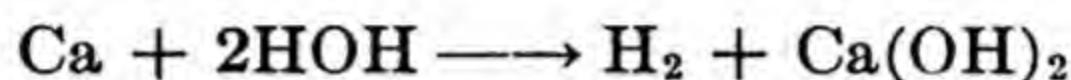


The reactions of calcium on water and of iron on water are shown in the following equations:

WORD EQUATION:

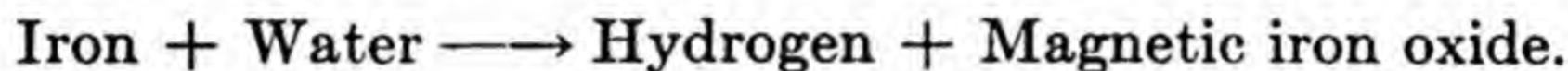


FORMULA EQUATION:



Calcium has a valence of 2; hence calcium hydroxide must be written $\text{Ca}(\text{OH})_2$.

WORD EQUATION:



FORMULA EQUATION:



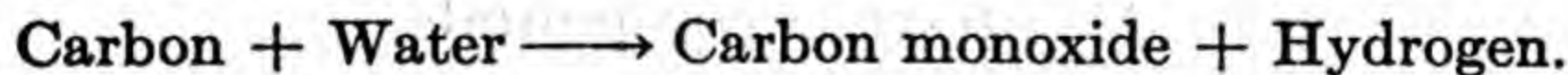
BALANCED EQUATION:



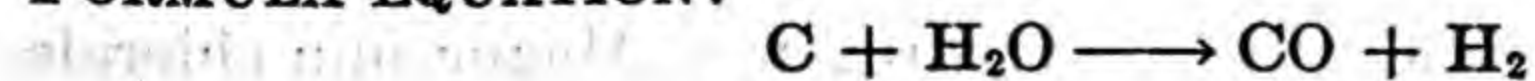
Iron drives out all the hydrogen from the water molecule, forming, with the oxygen, magnetic iron oxide, Fe_3O_4 .

The reaction between red-hot carbon (coke) and steam may also be considered as a replacement reaction.

WORD EQUATION:



FORMULA EQUATION:



BALANCED EQUATION:

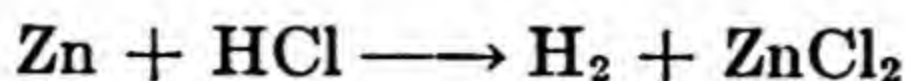


The action of acids on metals, for making hydrogen, also are replacement reactions:

WORD EQUATION:



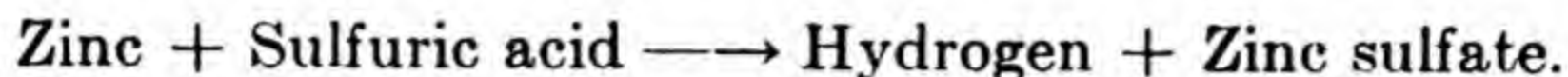
FORMULA EQUATION:



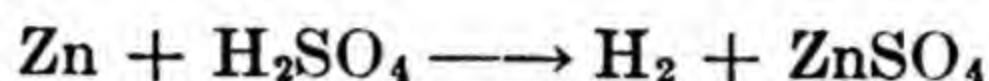
BALANCED EQUATION:



WORD EQUATION:



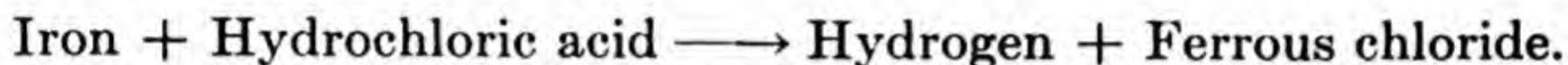
FORMULA EQUATION:



BALANCED EQUATION:



WORD EQUATION



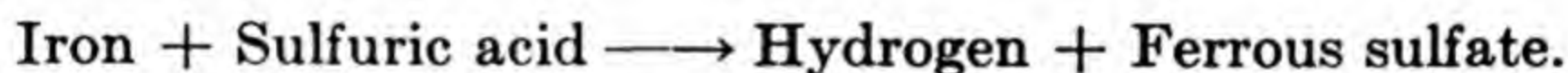
FORMULA EQUATION:



BALANCED EQUATION:



WORD EQUATION:



FORMULA EQUATION:



BALANCED EQUATION:



Iron has a valence of 2 in ferrous compounds.

WORD EQUATION:



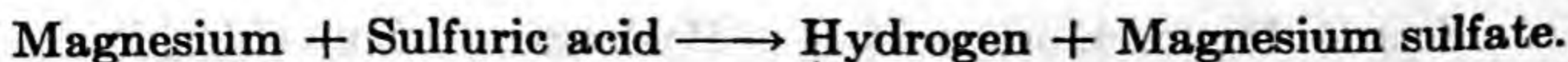
FORMULA EQUATION:



BALANCED EQUATION:



WORD EQUATION:



FORMULA EQUATION:



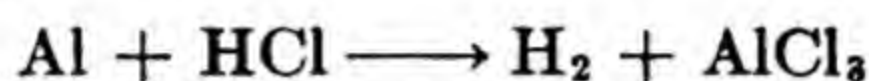
BALANCED EQUATION:



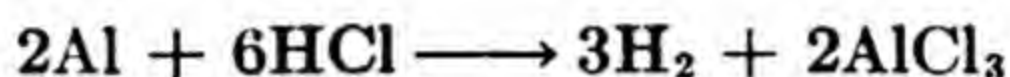
WORD EQUATION:

Aluminum + Hydrochloric acid \longrightarrow Hydrogen + Aluminum chloride.

FORMULA EQUATION:



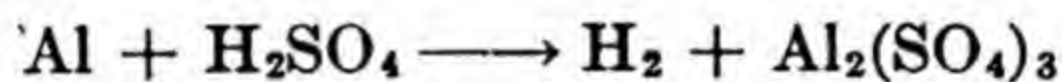
BALANCED EQUATION:



WORD EQUATION:

Aluminum + Sulfuric acid \longrightarrow Hydrogen + Aluminum sulfate.

FORMULA EQUATION:



BALANCED EQUATION:



The reduction of a metallic oxide by hydrogen gas is another example of replacement:

WORD EQUATION:

Copper oxide + Hydrogen \longrightarrow Copper + Water.

FORMULA EQUATION:



BALANCED EQUATION:



WORD EQUATION:

Ferrous oxide + Hydrogen \longrightarrow Iron + Water.

FORMULA EQUATION:



BALANCED EQUATION:



WORD EQUATION:

Magnetic iron oxide + Hydrogen \longrightarrow Iron + Water.

FORMULA EQUATION:



BALANCED EQUATION:



WORD EQUATION:

Zinc oxide + Hydrogen \longrightarrow Zinc + Water.

FORMULA EQUATION:



BALANCED EQUATION:



Double decomposition. The method for making hydrogen peroxide by the action of sulfuric acid on barium peroxide is an example of double decomposition. Double decomposition involves the changing of partners during the reaction

WORD EQUATION:

Barium peroxide + Sulfuric acid \longrightarrow Hydrogen peroxide + Barium sulfate

FORMULA EQUATION:



BALANCED EQUATION:



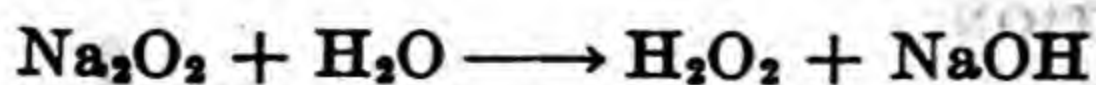
The first step in the reaction between hydrogen peroxide and water may be considered as a double decomposition. The second step is a simple decomposition.

WORD EQUATIONS:

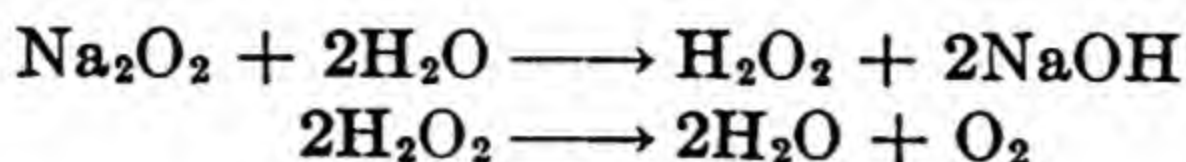
Sodium peroxide + Water \longrightarrow Hydrogen peroxide + Sodium hydroxide.

Hydrogen peroxide \longrightarrow Water + Oxygen.

FORMULA EQUATIONS:



BALANCED EQUATIONS:

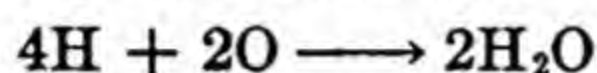


Questions and Exercises

1. What is meant by the following equation?



Is there any objection to writing it in this form?



2. Is sodium destroyed in the reaction between sodium and water?

3. Balance the following equations:

- (a) $\text{Li} + \text{HCl} \longrightarrow \text{LiCl} + \text{H}_2$
 (b) $\text{Mg} + \text{HCl} \longrightarrow \text{MgCl}_2 + \text{H}_2$
 (c) $\text{Cu} + \text{O}_2 \longrightarrow \text{CuO}$
 (d) $\text{MgO} + \text{H}_2 \longrightarrow \text{Mg} + \text{H}_2\text{O}$
 (e) $\text{O}_2 \longrightarrow \text{O}_3$

4. What things must you remember when you write an equation?

5. Why should a chemical equation be balanced?

6. To which of the four groups or types of chemical reactions does each of the following belong?

- (a) $2\text{Cu} + \text{O}_2 \longrightarrow 2\text{CuO}$
 (b) $\text{AgNO}_3 + \text{HCl} \longrightarrow \text{AgCl} + \text{HNO}_3$
 (c) $2\text{Al} + 6\text{HOH} \longrightarrow 3\text{H}_2 + 2\text{Al}(\text{OH})_3$
 (d) $\text{C}_{12}\text{H}_{22}\text{O}_{11} \longrightarrow 12\text{C} + 11\text{H}_2\text{O}$
 (e) $2\text{Na} + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2 + \text{Na}_2\text{SO}_4$

7. Write the equation for the decomposition of sodium chlorate. (Sodium chlorate and potassium chlorate decompose in the same way.)

8. Balance the following equations, and state which of the four types of chemical reactions each equation represents.

- (a) $\text{Fe} + \text{S} \longrightarrow \text{FeS}$
 (b) $\text{Na}_2\text{O}_2 + \text{HCl} \longrightarrow \text{H}_2\text{O}_2 + \text{NaCl}$
 (c) $\text{C} + \text{O}_2 \longrightarrow \text{CO}$
 (d) $\text{Fe}_3\text{O}_4 + \text{H}_2 \longrightarrow \text{Fe} + \text{H}_2\text{O}$

9. Write the following equations:

- (a) preparation of oxygen by decomposing mercuric oxide;
 (b) action of sodium on water;
 (c) preparation of hydrogen from sulfuric acid and a metal;
 (d) action of calcium on water;
 (e) preparation of oxygen by the decomposition of hydrogen peroxide.

10. Write equations for:

- (a) the reduction of copper oxide by hydrogen;
 (b) the burning of sulfur in air;
 (c) the burning of carbon in oxygen;
 (d) the burning of iron in oxygen.

PART 2

Chemical Calculations

More uses of the formula of a compound. The formula of a compound, in addition to telling us the kind and number of atoms in the molecule of the substance, gives us a means of making various chemical calculations. For example, we may wonder just how much of the weight of a sample of water is due to the hydrogen in its molecules, and how much of the weight is due to oxygen. If we know the formula for water, it is a simple matter to find the answer to this question. The result is usually expressed as the per cent of hydrogen and of oxygen in water; that is, as the number of grams of hydrogen and of oxygen in 100 g. of water. This is called the *percentage composition* of water.

How to find the percentage composition of a substance.

EXAMPLE 1. The formula for water is H_2O . Since the molecular weight of any substance is the sum of the weights of the atoms in its molecule, the molecular weight of water is 18.

$$\text{Formula} = \text{H}_2\text{O}.$$

$$\text{Molecular weight} = (2 \times 1) + 16 = 18.$$

There are, therefore, 2 parts by weight of hydrogen in every 18 parts of water, and 16 parts of oxygen in every 18 parts of water; or, we may say $\frac{2}{18}$ of water is hydrogen and $\frac{16}{18}$ of water is oxygen. To find the per cent of hydrogen in water, we multiply $\frac{2}{18}$ by 100. The per cent of oxygen is found in the same way, by multiplying $\frac{16}{18}$ by 100.

$$\text{Per cent of H} = \frac{2}{18} \times 100 = 11.1.$$

$$\text{Per cent of O} = \frac{16}{18} \times 100 = 88.9.$$

EXAMPLE 2. Let us calculate the percentage composition of sulfuric acid.

$$\text{Formula} = \text{H}_2\text{SO}_4.$$

$$\text{Molecular weight} = (2 \times 1) + 32 + (4 \times 16) = 98.$$

$$\text{Per cent of H} = \frac{2}{98} \times 100 = 2.04.$$

$$\text{Per cent of S} = \frac{32}{98} \times 100 = 32.65.$$

$$\text{Per cent of O} = \frac{64}{98} \times 100 = 65.31.$$

EXAMPLE 3. Sometimes we are interested in the percentage of only one part of a substance, as the per cent of water of crystallization in a hydrate. Let us find the per cent of water in blue vitriol. The water in a hydrate is actually part of the molecule. Its weight must therefore be included in the molecular weight of the substance. The weight of water in the molecule is *added* to the weight of the remainder of the molecule.

$$\text{Formula} = \text{CuSO}_4 \cdot 5\text{H}_2\text{O}.$$

$$\text{Molecular weight} = 63.6 + 32 + (4 \times 16) + (5 \times 18) = 249.6.$$

$$\text{Per cent of H}_2\text{O} = \frac{90}{249.6} \times 100 = 36.05.$$

The determination of the formula of a substance when the percentage composition is known. The formula of a substance can be determined from its percentage composition. This is the reverse of the procedure outlined above. When a new compound is discovered, the chemist analyzes it and finds out the weight of each element of which it is composed. If he is also able to determine the molecular weight of the compound by some of the methods to be described later, he can calculate the formula.

1. Calculation of the formula when the molecular weight is known.

EXAMPLE 1. Let us calculate the formula of sulfuric acid. It has a molecular weight of 98, and the percentage composition given above. Since the whole molecule weighs 98, and hydrogen composes 2.04 per cent of this, the weight of hydrogen in the molecule is

$$98 \times 0.0204 = 2.$$

Since one atom of hydrogen weighs 1, and $2 \div 1 = 2$, there must be two atoms of hydrogen in a molecule of sulfuric acid.

Sulfur makes up 32.65 per cent of the molecule; therefore the weight of sulfur is

$$98 \times 0.3265 = 32.$$

One atom of sulfur weighs 32, and $32 \div 32 = 1$; hence there is one atom of sulfur in the molecule.

Sulfuric acid is 65.31 per cent oxygen.

$$98 \times 0.6531 = 64.$$

Since the atomic weight of oxygen is 16, and $64 \div 16$ is 4, there must be four atoms of oxygen in one molecule of sulfuric acid. We can now write its formula, H_2SO_4 .

In other words, to determine the formula of a substance when its molecular weight and percentage composition are known, we apply the following method:

1. Multiply the molecular weight of the compound by the per cent of each of its constituent elements.

2. Divide each product by the atomic weight of the given element. This operation gives the number of atoms of each element in a molecule of the compound.

3. Write the formula, using the symbols of the elements and the appropriate numbers.

EXAMPLE 2. We shall apply this method in finding the formula of ammonia.

Molecular weight	= 17.
Per cent of N	= 82.35.
Per cent of H	= 17.65.
Part of molecular weight due to N	= $17 \times 0.8235 = 14.$
Part of molecular weight due to H	= $17 \times 0.1765 = 3.$
Number of atoms of N	= $14 \div 14 = 1.$
Number of atoms of H	= $3 \div 1 = 3.$
Formula = NH_3 .	

2. *Calculation of the formula when the molecular weight is not known.* It is often impossible to determine the molecular weight of the substance whose formula is desired. In these cases the ratio of the number of atoms of the different elements may be determined, and the simplest, or *empirical*, formula of the compound is written. This may be the true formula, but often the true molecular weight of the substance is two or more times that represented by the empirical formula.

Let us calculate the simplest formula for a substance which has the following percentage composition: Na, 32.40 per cent; S, 22.54 per cent; O, 45.07 per cent.

Since we do not know the molecular weight of the substance, it is convenient to assume that we have 100 parts of the compound. Then we proceed as follows:

Part of 100 due to Na	= $100 \times 0.3240 = 32.40.$
Part of 100 due to S	= $100 \times 0.2254 = 22.54.$
Part of 100 due to O	= $100 \times 0.4507 = 45.07.$
Number of atoms of Na in 100 parts	= $32.40 \div 23 = 1.409.$
Number of atoms of S in 100 parts	= $22.54 \div 32 = 0.704.$
Number of atoms of O in 100 parts	= $45.07 \div 16 = 2.818.$

No compound can contain less than one atom, because an atom is the smallest part of the element which takes part in chemical reactions. Therefore, 0.704 parts of S, which is the

smallest quotient obtained, must represent at least one atom. We divide this into the above quotients:

$$\text{Number of atoms of S in the molecule} = 0.704 \div 0.704 = 1.$$

$$\text{Number of atoms of Na in the molecule} = 1.409 \div 0.704 = 2.$$

$$\text{Number of atoms of O in the molecule} = 2.818 \div 0.704 = 4.$$

$$\text{Empirical formula} = \text{Na}_2\text{SO}_4$$

Assuming 100 parts of the substance in the beginning of the calculation amounts to the same thing as dividing the per cent of each element by its atomic weight in order to determine the relative number of atoms.

In general, the method for calculating the simplest formula of a compound when its percentage composition is given but its molecular weight is unknown is as follows:

1. Divide the number representing the per cent of each element (or its part out of 100 parts) by the atomic weight of the element.

2. Obtain the "whole-number ratio." This may usually be done by dividing each quotient by the smallest one, but it is sometimes necessary to find the greatest common divisor of all the quotients and then divide each quotient by that number.

3. Write the formula, using the numbers found in (2) as the subscripts of the symbols of the respective elements.

Another example is presented below in tabular form:

Element	Per cent in compound	Atomic weight	Per cent divided by atomic weight	Whole-number ratio	Simplest formula
Hydrogen.....	2.04	1	2.04	2	H ₂
Sulfur.....	32.65	32	1.02	1	S
Oxygen.....	65.31	16	4.08	4	O ₄

Calculations involving substances appearing in an equation. Just as the formula of a substance gives us a means of finding the relative weights of the elements in a compound, so a chemical equation composed of formulas gives us a means of determining the relative weights of the substances taking part in the reaction and of the products formed. This relation must be known before we attempt to make any substance in the laboratory. It is just as important as the use of a recipe in the kitchen. If we were to

attempt to make a cake with no knowledge whatever concerning the proper proportions of the ingredients, the result of the consumer might be disastrous. If we wish to make enough hydrogen in the laboratory to fill a balloon, using zinc and sulfuric acid, we should first know the ratio in which these two substances react, and the weight or volume of hydrogen which can be obtained from certain weights of zinc and of sulfuric acid. Otherwise the result might be just as bad as in the case of the cake.

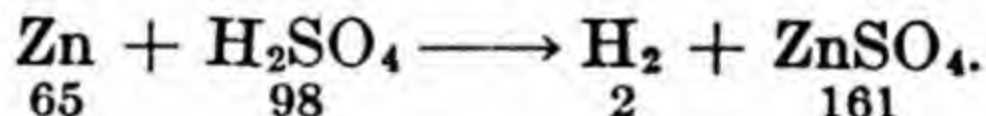
EXAMPLE 1. Let us suppose that our balloon requires 100 g. of hydrogen to fill it completely. How much zinc and how much sulfuric acid shall we use in order to make the 100 g. of hydrogen?

From our chemical equation for the reaction between zinc and sulfuric acid, we can determine the relative weights of the zinc and sulfuric acid which are used and of the hydrogen and zinc sulfate formed during the reaction. This relationship holds true whether we are weighing our substances in grams, pounds, or tons, or in any other units of weight.

We first write the balanced equation for the reaction



Under each formula we write the molecular weight, multiplied by the coefficient or number in front of the formula:



The coefficient of each of the substances in this equation is 1.

Our equation now tells us that when 65 g. (or lb., etc.) of zinc reacts with 98 g. of sulfuric acid, 2 g. of hydrogen and 161 g. of zinc sulfate are formed. If 65 g. of zinc with a sufficient weight of sulfuric acid yields 2 g. of hydrogen, how many grams of zinc must we use in order to make 100 g. of hydrogen?

Since we are required to make more hydrogen than is represented in the equation (100 g. instead of 2 g.), we must start with more zinc, or $\frac{100}{2}$ times as much zinc:

$$\frac{100}{2} \times 65 = 3250 \text{ g.}$$

The weight of zinc necessary to produce 100 g. of hydrogen is 3250 g. Or, if we wish to work the problem by proportion,

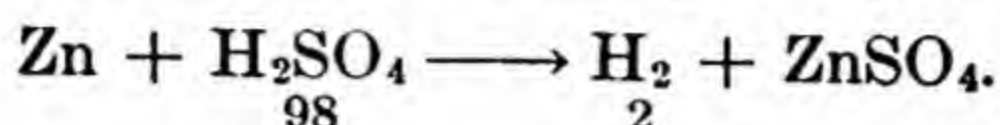
$$\frac{65}{x} = \frac{2}{100}.$$

The algebraic equation is solved for x :

$$2x = 6500; \quad x = 3250 \text{ g.}$$

The weight of zinc necessary to make 100 g. of hydrogen is 3250 g.

In the same way we solve for the weight of sulfuric acid which we must use with the 3250 g. of zinc to make 100 g. of hydrogen:



$$\frac{100}{2} \times 98 = 4900 \text{ g.}$$

It required 98 g. of sulfuric acid to make 2 g. of hydrogen and we must use more sulfuric acid if we wish to make 100 g. of hydrogen, ($\frac{100}{2}$ times as much).

If we prefer to solve the problem by proportion,

$$\frac{98}{x} = \frac{2}{100}; \quad 2x = 9800; \quad x = 4900 \text{ g.}$$

We might also wish to know the weight of zinc sulfate which is formed at the same time. Obviously more zinc sulfate will be formed when we make 100 g. of hydrogen than was formed when 2 g. of hydrogen was generated. The proportion is now formed between the weights of hydrogen and zinc sulfate:

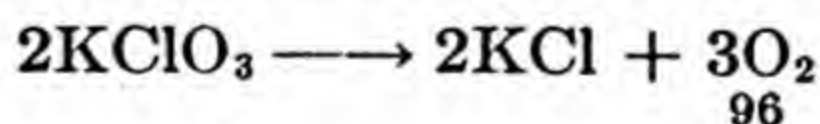


The solution is

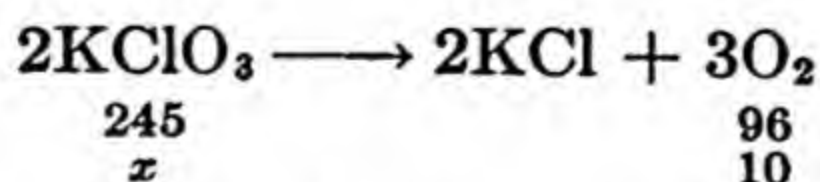
$$\frac{100}{2} \times 161 = 8050 \text{ g. ZnSO}_4.$$

EXAMPLE 2. Let us calculate the weight of potassium chlorate required to produce 10 g. of oxygen.

1. Write the balanced equation and place under each formula the weight of the compound represented by the formula:



2. Place below these numbers the corresponding required quantities, using x for the unknown:



3. Since we wish to make only 10 g. of oxygen, instead of 96 g. as represented in the equation, it is obvious that we should start with *less* than 245 g. of potassium chlorate. Hence the weight of potassium which we must use is

$$\frac{10}{96} \times 245 = 25.5 \text{ g.}$$

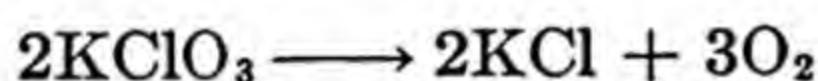
It requires, then, 25.5 g. of potassium chlorate to make 10 g. of oxygen.

Gram-molecular weight or mole. The weight of a single molecule of a substance is a unit too small for practical use. The chemist, therefore, has adopted a name for an assemblage of molecules having a weight, in grams, equal to the molecular weight of the substance. We call this quantity a gram molecule or a mole of the substance. This unit of weight may be used when we are dealing with either gases, liquids, or solids. Thus, one mole of helium is 4 g. of the gas. One mole of hydrogen is 2 g. of hydrogen; the weight of one mole of oxygen is 32 g., and of one mole of carbon dioxide, 44 g. Likewise, a mole of water weighs 18 g.; and a mole of sugar, $C_{12}H_{22}O_{11}$, weighs $(12 \times 12) + (22 \times 1) + (11 \times 16) = 342$ g. Since we usually represent the molecule of a solid element by its symbol, considering the element monatomic, the weight of one mole of a solid element is its *gram-atomic* weight. Hence a mole of zinc weighs 65 g.; a mole of iron, 56 g.; and a mole of sulfur, 32 g. A mole of any substance contains 6.06×10^{23} molecules of the substance. This number is known as Avogadro's number.

We may say, then, that when zinc and sulfuric acid react to form hydrogen and zinc sulfate, one mole of zinc reacts with one mole of sulfuric acid to give one mole of hydrogen and one mole of zinc sulfate:



Similarly, in the decomposition of potassium chlorate, we say that *two moles* of potassium chlorate yield *two moles* of potassium chloride and *three moles* of oxygen:



The number of moles is always equal to the number in front of the formula for each substance expressed in a *balanced* equation. The number of moles of the substance, multiplied by the molecular weight in grams, is equal to the number of grams of the substance taking part in the reaction as expressed by the balanced equation.

The equivalent weight. Another unit of weight often used, especially by analysts, is the equivalent weight. *The equivalent of an element is defined as the weight in grams of the element which combines with or displaces one gram of hydrogen.* For example, when hydrogen and chlorine combine to form hydrogen chloride, HCl, 35.5 grams of chlorine reacts with 1 gram of hydrogen. The equivalent weight of chlorine is, therefore, 35.5. In sodium chloride, NaCl, 23 grams of sodium are combined with 35.5 grams of chlorine, which is one equivalent of that element. Hence the equivalent weight of sodium is 23. We might reach the same conclusion by saying that 23 grams of sodium take the place of 1

gram of hydrogen when sodium chloride is formed by the action of sodium on hydrochloric acid. Since 23 grams of sodium have replaced 1 gram of hydrogen, 23 grams is the equivalent weight of sodium.

Hydrogen and oxygen combine in water in the ratio of 2 to 16 by weight; 16 g. of oxygen combine with 2 g. of hydrogen; hence the equivalent weight of oxygen is one-half the atomic weight, or 8 g.

When hydrochloric acid acts on magnesium, the following equation represents the reaction:



It can be seen that 24 grams of magnesium liberate 2 grams of hydrogen; 12 g. of magnesium, therefore, will liberate 1 g. of hydrogen, making the weight of an equivalent of magnesium equal to 12 g.

In general, the equivalent weight of a monovalent element is the same as its atomic weight. The equivalent weight of a divalent element like magnesium, zinc, or oxygen is one-half its atomic weight. A trivalent element has an equivalent weight which is one-third of its atomic weight.

Since a radical is a group of elements that acts like a single element in ordinary chemical reactions, we may also speak of the equivalent weight of a radical. In sodium hydroxide, NaOH, 17 g. of the radical OH are combined with 23 g. of sodium, which is one equivalent of sodium. The equivalent weight of the OH radical, therefore, is 17 g. Similarly, 96 g. of the sulfate radical combine with 2 g. of hydrogen in forming sulfuric acid, H_2SO_4 . The weight of an equivalent of the sulfate radical, then, is $\frac{1}{2} \times 96 = 48$ g. The equivalent weight of aluminum chloride, AlCl_3 , is one-third its molecular weight, or $\frac{1}{3} \times 133.5$ g., since this weight of aluminum chloride contains 9 g., or 1 equivalent of aluminum, and 35.5 g. or one equivalent of chlorine.

Questions and Exercises

1. From the formula for sodium chloride, calculate the per cent of sodium and chlorine in the compound.
2. From the formula for sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, calculate its percentage composition.
3. What is the percentage composition of hydrogen peroxide?
4. Calculate the percentages of oxygen in the following compounds: potassium bromate, KBrO_3 ; manganese dioxide, MnO_2 ; potassium nitrate, KNO_3 ; nitric acid, HNO_3 .
5. Calculate the percentage of iron in each of the following oxides of iron: ferrous oxide, FeO ; ferric oxide, Fe_2O_3 .

6. What weight of hydrogen is present in 10 tons of pure nitric acid, HNO_3 ?
7. Calculate the percentage of sulfur in crystallized copper sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.
8. What is the percentage of water of crystallization in washing soda, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$?
9. Calculate the amount of potassium chlorate necessary to liberate 20 g. of oxygen.
10. (a) How many grams of zinc are necessary to liberate 10 g. of hydrogen?
(b) How many grams of sulfuric acid will be required to liberate 10 g. of hydrogen?
(c) How many grams of zinc sulfate will be formed at the same time?
11. Calculate the amount of zinc and the amount of hydrochloric acid used, and the amount of zinc chloride formed, when 1 g. of hydrogen is liberated.
12. Calculate the weight of chlorine and the weight of sodium in 1 lb. of sodium chloride, NaCl .
13. What weight of mercuric oxide, HgO , is required to yield 16 g. of oxygen?
14. A piece of zinc weighing 6.5 g. was burned in air. The white powder which was formed (zinc oxide) weighed 8.1 g. What weight of oxygen combines with 6.5 g. of zinc? What is the per cent of oxygen in zinc oxide?
15. Calculate the per cent of each element in (a) zinc chloride, ZnCl_2 , (b) sodium sulfate, Na_2SO_4 , (c) potassium chlorate, KClO_3 .
16. A compound having a molecular weight of 100 consists of calcium, 40 per cent; carbon, 12 per cent; and oxygen, 48 per cent. Write its formula.
17. What weight of oxygen can be obtained from 50 g. of potassium chlorate?
18. Iron decomposes steam as indicated by the equation



What weight of iron must be used to supply 50 lb. of hydrogen?

19. Calculate the per cent of hydrogen in ammonia, NH_3 .
20. Find the weight of chlorine in 15 lb. of potassium chlorate, KClO_3 .
21. Write the simplest formula for a compound having this composition: calcium, 29.40 per cent; sulfur, 23.56 per cent; oxygen, 47.04 per cent.
22. Complete the following table:

Element	Per cent in compound	Atomic weight	Per cent divided by atomic weight	Whole-number ratio	Simplest formula
Potassium	45.88				
Nitrogen	16.47				
Oxygen	37.65				

23. Washing soda may be purchased in the form of a powder having the formula Na_2CO_3 , or in the form of crystals corresponding to the formula $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. Which is the more expensive source of Na_2CO_3 : the crystals at 6 cents a pound or the powder at 7 cents a pound?

24. The molecular weight of benzene is 78. It is 92.3 per cent carbon and 7.7 per cent hydrogen. Find its formula.

25. The molecular weight of a certain gas is 34. The gas is 94.12 per cent sulfur and 5.88 per cent hydrogen. What is its formula?

26. A compound contains 58.8 per cent of barium, 13.75 per cent of sulfur, and 27.45 per cent of oxygen. Find its formula.

27. What is the empirical formula of the substance which contains 2.74 per cent of hydrogen and 97.26 per cent of chlorine?

28. A sample of gas contains 27.27 per cent of carbon and 72.73 per cent of oxygen. Its molecular weight is 44. What is its formula?

29. Calculate the formula of the substance which has the following composition: sodium, 36.5 per cent; hydrogen, 0.8 per cent; phosphorus, 24.6 per cent; oxygen, 38.1 per cent.

30. Calculate the weight of one mole of each of the following substances: (a) NaCl , (b) NH_3 , (c) HNO_3 , (d) H_2SO_4 , (e) Ne , (f) AlCl_3 , (g) Na_2SO_4 , (h) NaOH , (i) NH_4Cl , (j) $\text{C}_2\text{H}_5\text{OH}$.

31. Calculate the weight of one equivalent of (a) the nitrate radical in HNO_3 , (b) aluminum in AlCl_3 , (c) the ammonium radical in NH_4Cl , (d) the sulfate radical in Na_2SO_4 .

PART 3

Calculations Involving the Weights of Gases

The relative weights of equal volumes of gases. Although equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules, they do not weigh the same amount. A liter of oxygen weighs more than a liter of hydrogen, because each molecule of oxygen weighs more than a molecule of hydrogen.

An oxygen molecule is 16 times as heavy as a hydrogen molecule. Since a liter of each of these gases has in it the same number of molecules, we should expect the weight of a liter of oxygen to be 16 times as heavy as that of a liter of hydrogen, and this is true. A liter of oxygen weighs 1.429 g. and a liter of hydrogen weighs 0.09 g.

Similarly, a molecule of carbon dioxide is 22 times as heavy as a molecule of hydrogen. A liter of carbon dioxide, therefore, should weigh 22 times as much as a liter of hydrogen. This deduction is found to be true. A liter of carbon dioxide under standard conditions weighs 1.98 g.

The weights of equal volumes of gas are in the same ratio as their molecular weights.

A method for finding molecular weights of gases. If we wish to find the molecular weight of a gas, we can weigh 1 liter of it in the laboratory, and calculate its weight under standard conditions. We then divide this weight by 0.09, the weight of 1 liter of hydrogen. In this way we find out how many times heavier the gas is than hydrogen. This ratio is ordinarily called the *vapor density* of the gas. Since one molecule of hydrogen weighs 2, the vapor density multiplied by 2 gives us the weight of a molecule (the molecular weight) of the unknown gas. A problem will make this clear:

Wt. of liter of unknown gas under standard conditions = 1.64.

Wt. of 1 liter of hydrogen = 0.09.

Vapor density of gas = $\frac{1.64}{0.09} = 18.22$.

Molecular weight of gas = $2 \times 18.22 = 36.44$ g.

Gram-molecular volume. If 0.09 g. of hydrogen occupies 1 liter, what volume is occupied by 2 g. or one mole of hydrogen? For this calculation we will use the more exact value of 2.016 for the molecular weight of hydrogen. Dividing this number by the weight of one liter of the gas we obtain

$$\frac{2.016}{0.09} = 22.4 \text{ liters.}$$

One mole of hydrogen occupies a volume of 22.4 liters under standard conditions.

One liter of oxygen under atmospheric pressure and at 0°C. weighs 1.429 g. The volume occupied by 32 g. (one mole) of

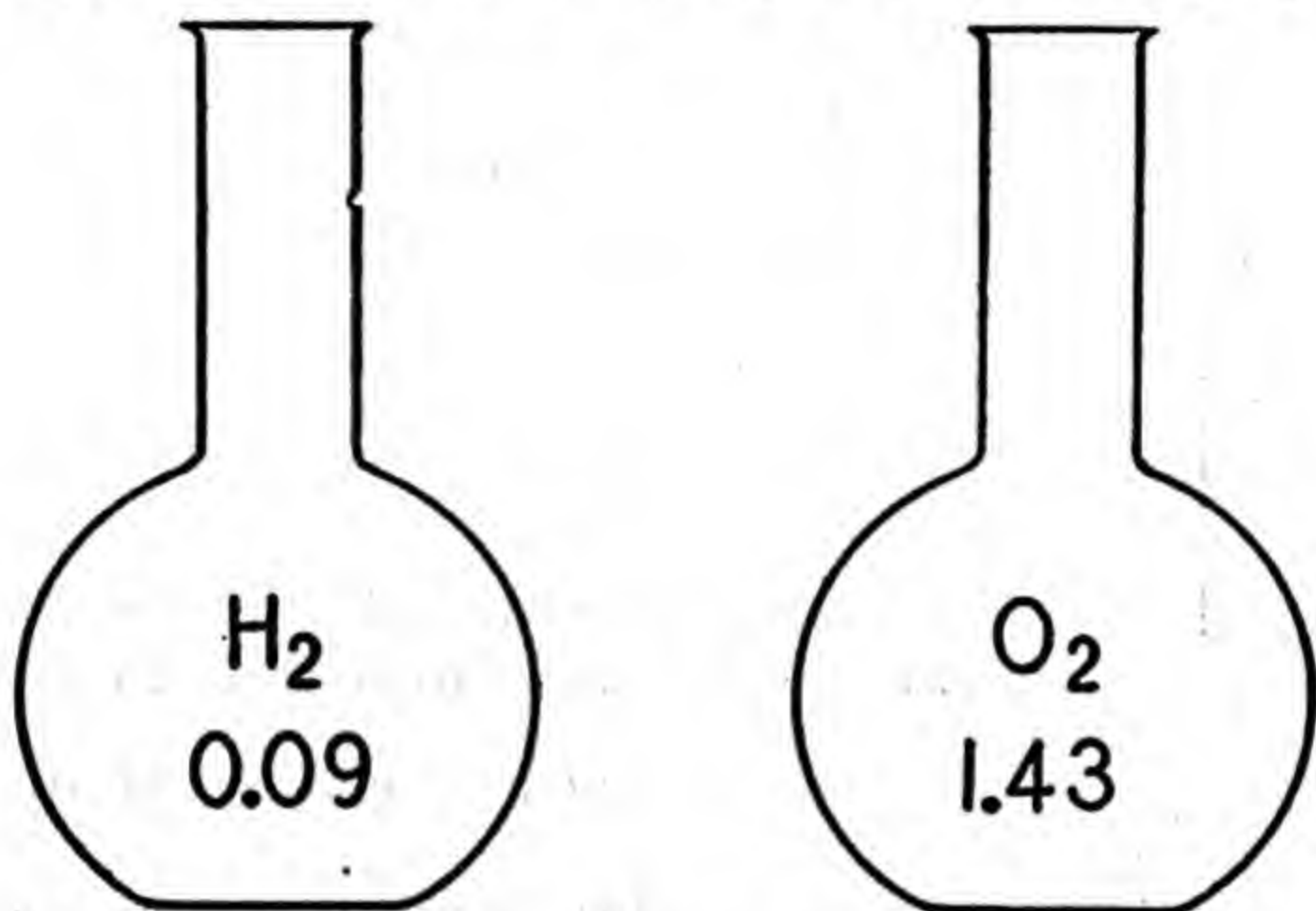


Fig. 102. A liter of oxygen weighs 16 times as much as a liter of hydrogen. Each flask contains the same number of molecules.

oxygen is $32 \div 1.429 = 22.4$ liters. Approximately the same volume is occupied by a mole of each of these gases. The value 22.4 liters is obtained for the volume of one mole of any other gas. This volume is called the gram-molecular volume, or the molal volume of a gas. *One mole (molecular weight in grams) of any gas occupies 22.4 liters measured under standard conditions of temperature and pressure.*

The number of molecules in 22.4 liters has been determined by several methods. This number is very close to 6×10^{23} molecules, which means the same as 6 followed by 23 ciphers.

Another method for finding the molecular weight of a gas. The fact that one mole of every gas occupies 22.4 liters provides us with a simple method of determining the molecular weight of gases. We merely have to find the weight of 22.4 liters of the gas. The molecular weight of a gas is numerically equal to the weight in grams of 22.4 liters of the gas at 0°C. and 1 atmosphere pressure.

It is not necessary to have a vessel which holds 22.4 liters of the gas for this determination. If 1 liter of the gas is available, its weight multiplied by 22.4 gives us the molecular weight. For example, 1 liter of carbon monoxide weighs 1.25 g. Therefore 22.4 liters weigh 22.4×1.25 , or 28 g. The molecular weight of carbon monoxide is therefore 28.

Frequently the chemist has at hand only a few cubic centimeters of the gas the molecular weight of which he wishes to determine. Perhaps the gas is bubbling very slowly from a spring, or it may be formed in small amounts during a chemical reaction. He does not need to wait until he has collected even 1 liter of the gas.

Let us suppose that he has only 10 cc. of the pure gas in a tube. The gas is weighed accurately, and is found to weigh 0.0154 g. If 10 cc. weigh this amount, 1 liter (1000 cc.) weighs $\frac{1000}{10}$, or 100 times as much, or

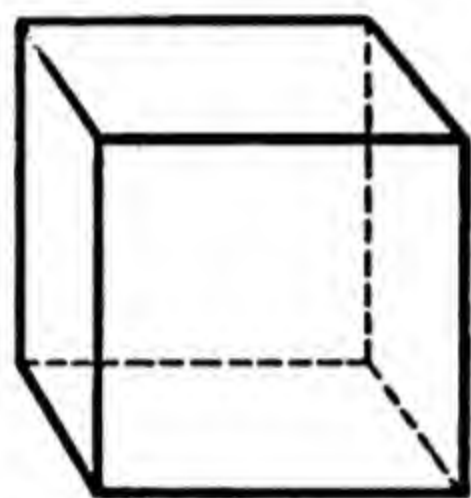


Fig. 103. A cube 11.1 in. on each edge has a capacity of 22.4 liters. This is the gram-molecular volume of any gas.

$$\frac{1000}{10} \times 0.0154 = 1.54 \text{ g.}$$

The molecular weight is the weight of 22.4 liters and is determined as before:

$$22.4 \times 1.54 = 34.49$$

The molecular weight of the gas is therefore 34.49 g.

To find the weight of 1 liter of a gas. Conversely, if we know the molecular weight of a gas, it is a simple matter to find the weight of 1 liter. For example, 22.4 liters of oxygen weigh 32 g. Therefore 1 liter of oxygen weighs $32 \div 22.4$ or 1.429 g.

Weight of another gas compared with that of air. We can calculate by means of these relations whether a gas is heavier or lighter than air. The ratio between the weight of a given volume of a gas and the weight of the same volume of air is called the *specific gravity* of the gas.

The weight of a liter of air, under standard conditions, is approximately 1.293 g. A gram-molecular volume of air weighs 22.4×1.29 , or 28.89 g. If the gram-molecular weight of a gas is *greater* than 28.89, the gas is heavier than air; if it is smaller, the gas is lighter than air.

The formula for ammonia is NH_3 . Its molecular weight is $14 + (3 \times 1)$, or 17. Its gram-molecular weight is therefore 17 g. Since this is less than 28.89, ammonia gas is lighter than air.

Questions and Exercises

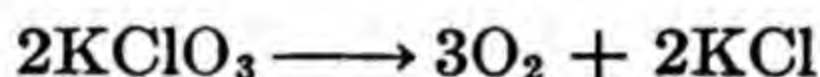
1. What is a gram molecule or mole of a substance?
2. What volume is occupied by a mole of any gas at 0°C . and 1 atmosphere pressure?
3. The molecular weight of methane gas, CH_4 , is 16. The molecular weight of hydrogen is 2. If 1 liter of hydrogen weighs 0.09 g., what is the weight of 1 liter of methane?
4. At 0°C . and 1 atmosphere, 1 liter of carbon dioxide gas weighs 1.965 g. Calculate the molecular weight of the gas.
5. Under standard conditions, 3 liters of a gas called carbon monoxide weigh 3.75 g. Calculate its molecular weight.
6. The formula of carbon monoxide is CO . Find the weight of 1 liter of the gas.
7. The weight of 22.4 liters of air at standard conditions is 28.89 g. Which of the following gases are heavier, and which are lighter, than air: (a) hydrogen chloride gas; (b) carbon dioxide; (c) oxygen; (d) chlorine; (e) nitrogen?
8. From the molecular weight of oxygen calculate the weight of 1 liter of the gas at 0°C . and 1 atmosphere.
9. At 0°C . and under 1 atmosphere pressure, 1 liter of water dissolves 0.07 g. of oxygen. How many liters of water are required to dissolve 1 mole of oxygen?
10. Acetylene has the formula C_2H_2 . What is the weight of 1 cc. of this gas at 0°C . and 1 atmosphere pressure?
11. One liter of liquid oxygen weighs 1130 g. How many liters of oxygen gas at 0°C . and atmospheric pressure can be obtained by evaporating a liter of liquid oxygen?
12. Calculate the weight of 1 liter of each of the following gases at standard conditions: (a) SO_2 ; (b) H_2S ; (c) NO ; (d) HBr ; (e) Cl_2 .
13. The weight of 250 cc. of a gas is 0.38 g. Calculate (a) its molecular weight; (b) its vapor density; (c) the weight of 1 liter.
14. The formula of a certain gas is HCN . Calculate (a) its molecular weight; (b) the weight of 1 liter; (c) its percentage composition by weight.
15. What is the molecular weight of a gas, 50 cc. of which weigh 0.076 g.?
16. Which is the heavier gas, (a) hydrogen chloride or oxygen; (b) oxygen or nitrogen; (c) ammonia or nitrogen?

PART 4

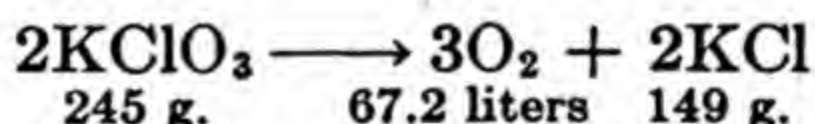
Calculations Involving Gram-molecular Volumes

Weight-volume problems. We have learned how to use chemical equations in calculating the *weight* relations between substances that enter into a reaction and the products formed. Frequently we are interested in the *volume* of a gas formed when a certain weight of a solid or liquid reacts. Such problems can be solved by making use of the gram-molecular volume of a gas.

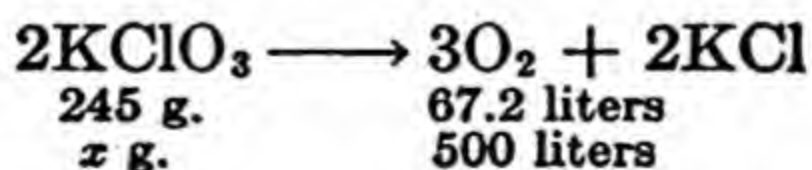
For example, let us calculate how many grams of potassium chlorate will be needed to make 500 liters of oxygen. As before, we write the balanced equation for the reaction:



It tells us that two moles of potassium chlorate, when heated, give three moles of oxygen and two moles of potassium chloride. We know that the volume of 1 mole of oxygen is 22.4 liters; therefore the 3 moles of oxygen represented in the equation occupy 3×22.4 , or 67.2 liters. We place under each formula, except the one for oxygen, the weight of the substance represented. Under the formula for oxygen we write the *volume* represented:



Below these numbers we write the corresponding required quantities, using x for the unknown. The letter x now represents the weight of potassium chlorate required to yield 500 liters of oxygen gas.

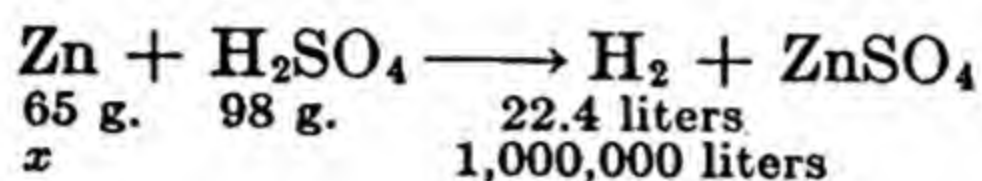


Solving the proportion,

$$x = \frac{500}{67.2} \times 245 = 1822 \text{ g.}$$

In order to produce 500 liters of oxygen, we must decompose 1822 g. of potassium chlorate.

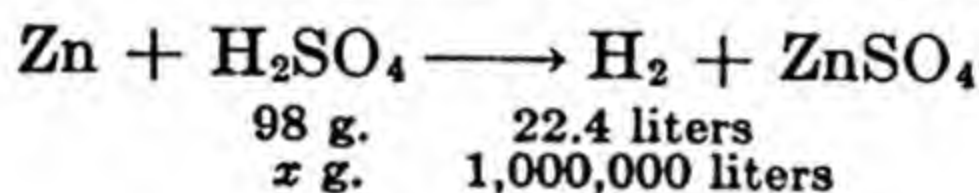
A common type of problem is to determine how many grams of zinc and how many grams of sulfuric acid will be required to make enough hydrogen to fill a balloon of given volume. Let us suppose that our balloon has a volume of 1,000,000 liters under standard conditions. We write the equation for the reaction, and the weights represented by the solid, zinc, and the liquid, sulfuric acid. We place under the formula of hydrogen the *volume* represented by the equation. This is 22.4 liters, since one mole of hydrogen appears in the balanced equation. Let us solve first for the weight of zinc required:



Then

$$x = \frac{1,000,000}{22.4} \times 65 = 2,901,785 \text{ g.}$$

We must place 2,901,785 g. of zinc in our hydrogen generator.
How much sulfuric acid shall we add to the zinc?



Then

$$x = \frac{1,000,000}{22.4} \times 98 = 4,375,000 \text{ g.}$$

If we pour 4,375,000 g. of sulfuric acid on 2,901,785 g. of zinc, enough hydrogen to fill our balloon will be produced.

Care must be taken, when working problems involving chemical equations, to use the same units to represent quantities placed under corresponding formulas. When the problem calls for the *volume* of a gas, the *volume* represented in the equation must be placed under the formula. When the *weight* of a gas is required, the *weight* of gas represented in the equation must be placed under the formula. The *unit* must be the same in the numerator and denominator of each ratio in the proportion. Failure to observe this will lead to an absurd result. It would make the proportion as meaningless as the following: If a pair of shoes costs \$10, how many hats can be purchased for \$100?

How to determine the formula of a gas. In Unit IV, Part 2, we learned how to determine the formula of a substance when the molecular weight and the percentage composition are known. Let us now find the correct formula for a gas when the weight of any volume and the percentage composition are known. The following example illustrates such a problem:

A gas is composed of carbon 85.71 per cent and hydrogen 14.29 per cent. At 0° and under 1 atmosphere of pressure, 1 liter of the gas weighs 1.26 g. Find its formula.

The molecular weight of the gas is $22.4 \times 1.26 = 28$. We then have:

Molecular weight	= 28.
Per cent of C	= 85.71.
Per cent of H	= 14.29.
Parts of molecular weight due to C	= $28 \times 0.8571 = 24$.
Parts of molecular weight due to H	= $28 \times 0.1429 = 4$.
Number of atoms of C	= $24 \div 12 = 2$.
Number of atoms of H	= $4 \div 1 = 4$.
Formula = C_2H_4 .	

Questions and Exercises

1. Calculate the amount of potassium chlorate necessary to liberate 67.4 liters of oxygen measured at standard conditions.

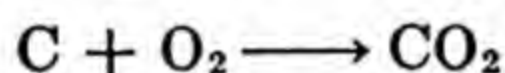
2. How many grams of zinc reacting with an excess of hydrochloric acid are necessary to liberate 10 liters of hydrogen?

3. How many grams of sulfuric acid reacting with iron are necessary to liberate 6 liters of hydrogen?

4. How many grams of $ZnSO_4$ are formed when 11.2 liters of hydrogen are formed by the following reaction?



5. Carbon burns in air, yielding carbon dioxide, as indicated by the equation



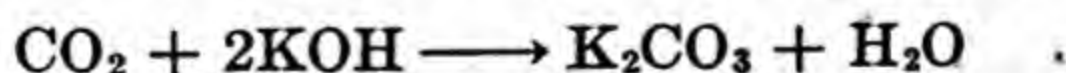
When 1 liter of oxygen is used, what volume of carbon dioxide is formed?

6. Sodium peroxide liberates oxygen from water according to the equation



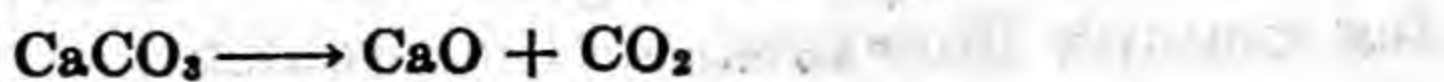
What weight of sodium peroxide is required to yield 30 liters of oxygen measured under standard conditions?

7. What weight of potassium hydroxide, KOH, is required to absorb 3.6 moles of carbon dioxide according to the following equation?



8. Calculate the amount of zinc and the amount of sulfuric acid used and the amount of zinc sulfate formed when 1 g. of hydrogen is formed by the equation shown in Exercise 4.

9. Calculate the weight of lime, CaO, and the volume of carbon dioxide, CO_2 , that may be obtained from a ton of limestone, $CaCO_3$.



10. A certain gas, under standard conditions, weighs 2.254 g. per liter. Its composition is carbon, 23.76 per cent; hydrogen, 5.94 per cent; and chlorine, 70.30 per cent. Write the formula of the compound.

11. A sample of potassium chlorate weighing 24.5 lb. was heated to generate oxygen. After heating, the residue weighed 16.5 lb. Was all the potassium chlorate decomposed?

12. What weight of zinc will dissolve in 300 g. of sulfuric acid? What volume of hydrogen will be liberated?

13. Methane is a gas having a molecular weight of 16. It is composed of carbon and hydrogen only. The atomic weight of carbon is 12.01. Write the formula of methane.

14. A gas is composed of 92.3 per cent carbon and 7.7 per cent hydrogen. The weight of 199.4 cc. under standard conditions is 0.70 g. What is the formula of the gas?

UNIT V

Group I of the Periodic Table: The Alkali Metals

PART 1

Sodium

The elements included in Group I of the Periodic Table show a remarkable resemblance to each other in all properties. They are called the alkali metals. These elements are lithium, sodium, potassium, rubidium, and cesium. The best known of these elements is sodium. We have had much to say about sodium chloride, and we should learn something about the elements of which common salt is composed. If we know the properties of sodium, we know something about all the members of the family of elements in Group I.

The alkali metals are so active chemically that they are separated with difficulty from their ores, and when they are obtained in the metallic state, they have a great tendency to react with other elements and form compounds again. Since each of these metals has one electron in the valence orbit, and gives

PHYSICAL PROPERTIES OF THE ALKALI METALS

	Lithium	Sodium	Potassium	Rubidium	Cesium
Symbol.....	Li	Na	K	Rb	Cs
Atomic weight.....	6.94	22.997	39.096	85.48	132.91
Atomic number.....	3	11	19	37	55
Melting Point, °C.....	179	97.5	63.5	39.0	28.4
Boiling point, °C.....	1372	892	774	679	690
Density, grams per cubic centimeter at 20°C.....	0.53	0.97	0.86	1.53	1.90
Isotopes.....	6, 7	23	39, (40), 41	85, 87	133
Electron structure:					
1st shell.....	2	2	2	2	2
2nd shell.....	1	8	8	8	8
3rd shell.....	—	1	8	18	18
4th shell.....	—	—	1	8	18
5th shell.....	—	—	—	1	8
6th shell.....	—	—	—	—	1

up the valence electron readily, it is not surprising that they occur in nature only as compounds.

On the other hand, the common metals like iron, copper, zinc, silver, and gold are familiar to all of us in useful and ornamental articles. Men learned to separate them from their ores and to make use of them centuries before hydrogen and oxygen were discovered. Once separated from their ores, they can easily be kept in the metallic state.

Occurrence and discovery of sodium. Sodium is one of the most abundant of the elements found on the earth. Nearly all rocks contain sodium in compound form. Sea water contains an enormous quantity of sodium chloride (2.5 per cent), and deposits of this salt formed from prehistoric oceans and salt lakes are found in most countries. Sodium itself is so active that it is never found in the free state, and it was not separated from any of its compounds until Sir Humphry Davy, in 1807, succeeded in preparing it by means of the newly discovered electric current. Placing the wires of his battery in melted sodium hydroxide (caustic soda), he saw a drop of the metal form on one of the wires. He was the first to obtain metallic sodium.

Commercial preparation of sodium. Sodium is prepared commercially by a modification of the same method which Davy employed—the electrolysis of fused (melted) sodium hydroxide, NaOH . Sodium is prepared commercially from fused sodium hydroxide with equipment such as that shown in Fig. 104. The whole container is made of iron, and the contents can be heated by a gas flame. At the negative electrode

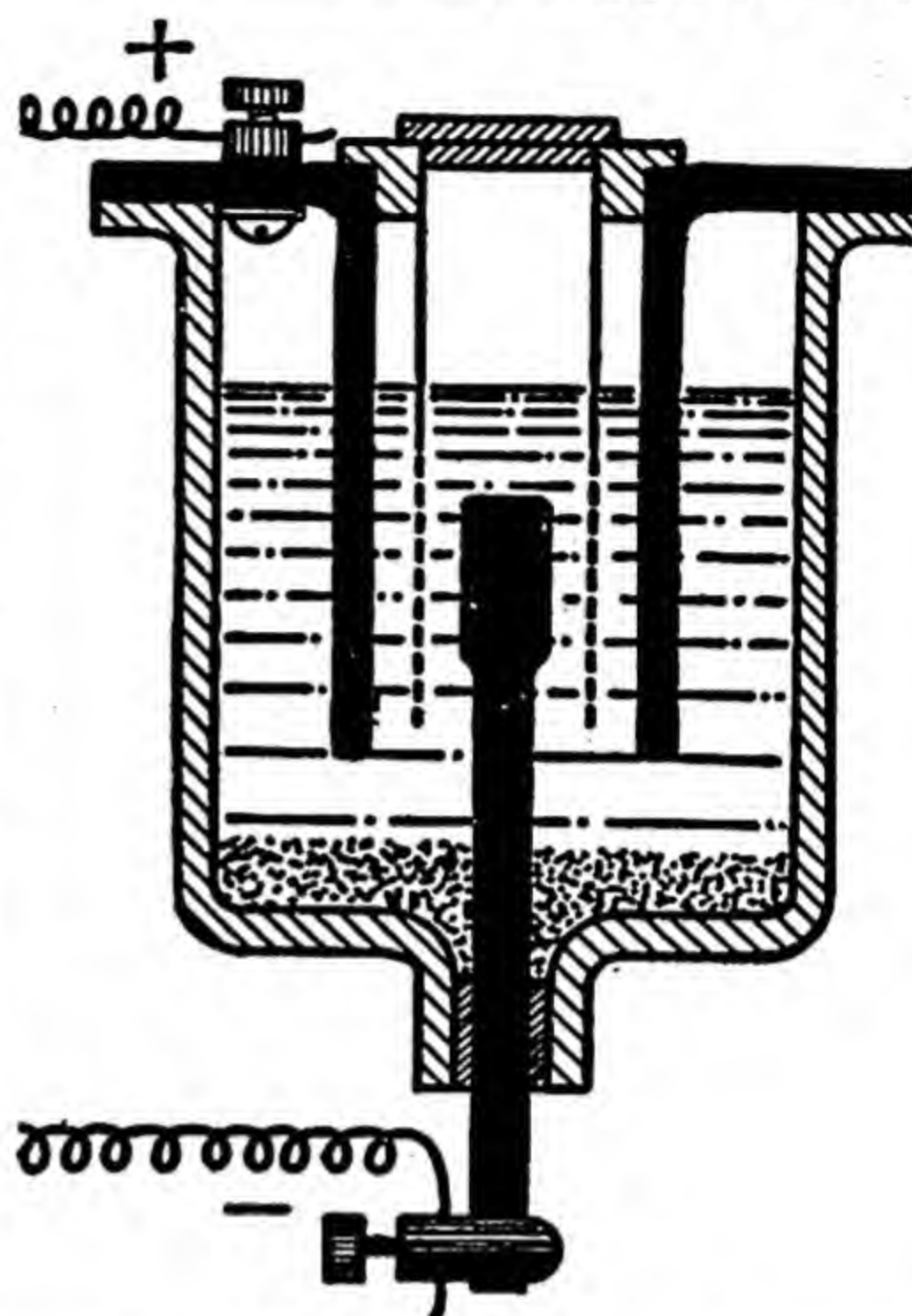
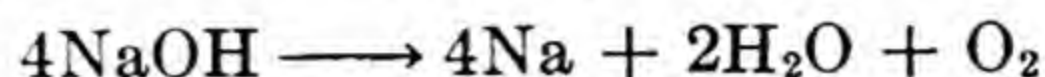


Fig. 104. Cross section of a cell devised by Castner for obtaining metallic sodium from fused sodium hydroxide. Sodium and hydrogen collect in a central chamber above the cathode (the cathode is marked $-$). Hydrogen escapes through a valve in the lid of the central cylinder. The sodium floats on the molten sodium hydroxide and is skimmed off from time to time. It is protected from the air by the atmosphere of hydrogen above it. Oxygen is liberated on the surfaces of iron anodes (marked $+$), and the gas escapes through an opening. Several anodes are suspended around the cathode and are kept from touching the cathode by a wire gauze cylinder. The heat generated by the electric current is usually sufficient to keep the hydroxide melted in the upper part of the apparatus, but burners may be used if necessary.

both hydrogen and sodium are liberated, and oxygen alone is evolved at the positive electrode. The equation for the main reaction is:



Hydrogen is liberated at the same time, for some of the water formed in the main reaction diffuses through the molten mass and, at the cathode, comes in contact with free sodium. This method for producing sodium is advantageous because of the relatively low melting point of sodium hydroxide ($318^\circ\text{C}.$). Sodium chloride

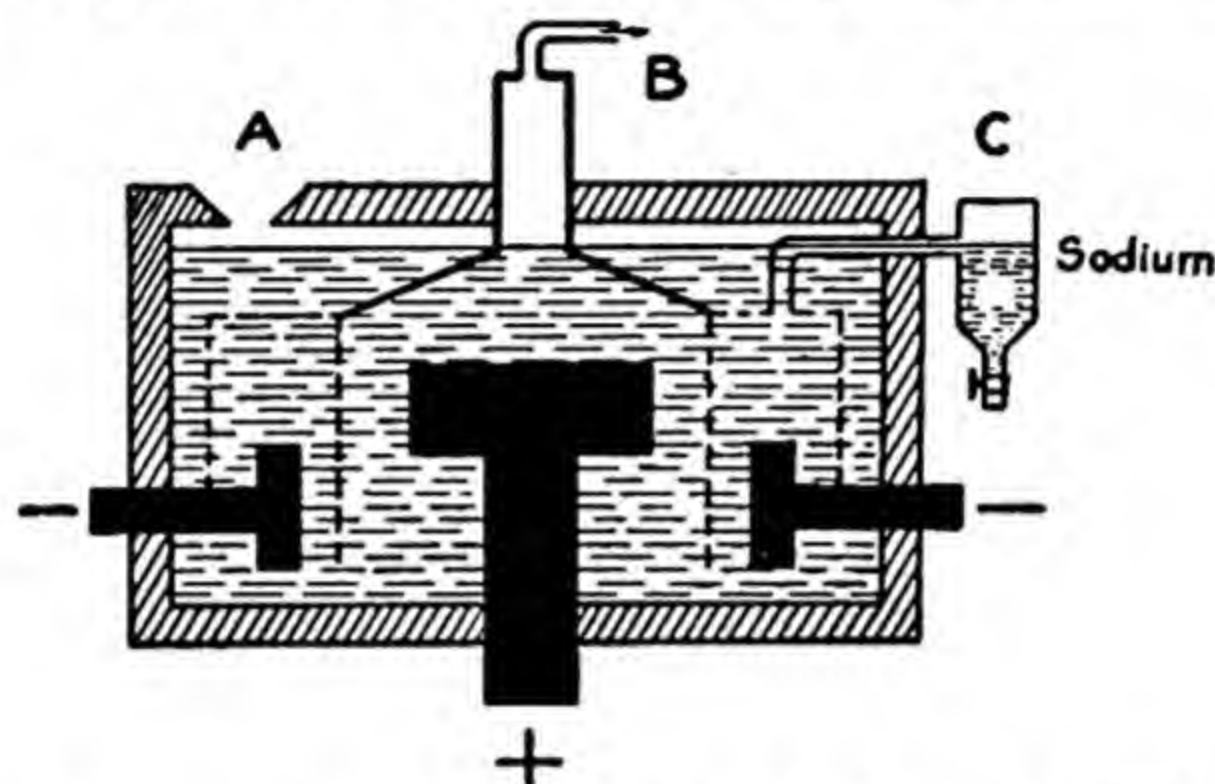


Fig. 105. Cross-section of the Downs cell for making sodium from sodium chloride. The box is made of iron, lined with fire brick. The graphite positive electrode projects through the bottom of the box. The negative electrode is a band of iron or copper which encircles the graphite electrode, being separated from it by a wire gauze. Sodium is produced at the negative electrode and flows into the receiver, C, from which it is removed from time to time. Chlorine, a valuable by-product, escapes from the apparatus through a pipe, B, over the positive electrode, where the chlorine is liberated. More sodium chloride is added at A from time to time, and is kept in the melted state through its resistance to the passage of the electric current.

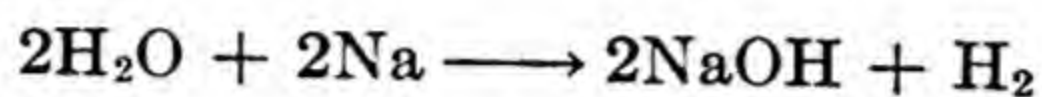
is a far cheaper source from which to obtain sodium than is the more costly sodium hydroxide, but its high melting point ($800^\circ\text{C}.$) presented so many difficulties that it was not used extensively for many years. However, by adding other salts to the sodium chloride, it is possible to obtain a mixture with a melting point as low as $600^\circ\text{C}.$ A mixture of salts always has a lower melting point than that of a pure salt. The Downs cell makes use of this principle, and most of the sodium is now made by this process, the electrolysis of fused sodium chloride.

Physical properties. Sodium is lighter than water. Its melting point is below the boiling point of water, and the metal itself is so soft that it can be cut very easily with a knife. It is

very malleable, it is a good conductor of electricity, and a freshly cut surface has a metallic luster like that of silver.

Chemical properties. Sodium is so active that it must be kept under kerosene or some other inert liquid. It reacts readily with both the oxygen and the water vapor in the air.

The preparation of hydrogen by the action of sodium on water has been described. In this reaction the sodium replaces one-half the hydrogen in the H_2O molecule, and sodium hydroxide and hydrogen are formed:



The sodium hydroxide formed is soluble in water, but it may be obtained in a pure state by evaporating the water.

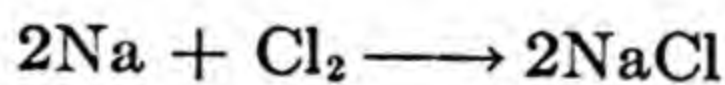
When freshly cut sodium is exposed to air containing water vapor, it immediately becomes coated with a layer of sodium hydroxide, and the surface loses its metallic luster. In perfectly dry air no reaction takes place at room temperature, but at a higher temperature sodium burns, reacting with the oxygen of the air to form the compound sodium peroxide, Na_2O_2 .

Sodium and its compounds impart a bright yellow color to a flame. If a platinum wire is dipped in sodium chloride, and then held in the flame of a Bunsen burner, a luminous yellow color results. This is used as a test for sodium compounds.

Sodium, as well as the rest of the alkali metals, reacts with acids to liberate hydrogen. This reaction is so violent that it is not safe to perform the experiment in the laboratory:



Sodium combines directly with chlorine, forming sodium chloride:



Uses of sodium. Although sodium is a good conductor of electricity, it cannot be utilized for that purpose in the form of exposed wires or cables. It oxidizes in the air far too rapidly. It also reacts energetically with the moisture in the air, and would disappear during the first rainstorm. Attempts are being made to use it as a conductor of electricity by enclosing it in air-tight, waterproof, hollow copper or iron tubes.

When sealed in a glass tube and vaporized by the electric current, sodium gives off a brilliant yellow light which does not cause a glare, and which is visible through fog and mist. These sodium vapor lamps, or sodium arcs, are being used for highway illumination in ever increasing numbers. The Golden Gate and San Francisco Bay Bridges in California are lighted by this means.

Sodium is also used in making useful compounds, such as sodium cyanide and sodium peroxide; in the preparation of indigo, certain



Fig. 106. Sodium vapor lamps are used to illuminate the traffic lanes on the San Francisco Bay Bridge.

perfumes, and tetraethyl lead; and as a catalyst in making some of the synthetic rubbers.

Compounds of Sodium

Sodium chloride. Sodium chloride is one of the most important salts in the world. It is essential as an article of diet. Digestive and other normal bodily functions are dependent upon its presence in the blood stream and in the tissues of the body. In earlier times salt was used for money by some of the tribes of India. It was weighed or measured to pay differences due in their barter, or exchange of commodities. Taxes for revenue have been levied on salt in many lands, for salt is one of the few things that even the poorest people will buy.

Even in the solid state sodium chloride is ionized, that is, the chlorine atoms have taken electrons from the sodium atoms. In a crystal of salt (see Fig. 19, page 24), each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. The units of which the crystal is built are the ions and not sodium chloride molecules, but, for convenience, we write the formula NaCl for common salt, although this formula implies that the atoms are held together in pairs.

Sodium chloride is found extensively on the earth. This salt comprises about 2.5 per cent of ocean water. It is found also in large deposits in the form of rock salt, in many localities. There is enough salt in Kansas, Oklahoma, and Texas to supply the needs

of the United States, at the present rate of consumption, for a million years.

Sodium chloride, as found in nature, has many other substances mixed with it, and it must be purified before it is used in food. The crude salt is first separated from insoluble impurities by dissolving the salt in water. The clear solution is run off from the insoluble matter, and the solvent is evaporated until a large part of the salt has crystallized out. Solar heat is usually employed for this purpose to avoid the expense of fuel.

The salt obtained after one crystallization still contains small amounts of other substances such as magnesium chloride and calcium chloride. Both of these salts absorb moisture on a damp day, causing difficulty in pouring or shaking the salt from a container. Pure salt does not get wet under ordinary atmospheric conditions.

Sodium sulfate. This salt occurs both in solution in ground waters and in the form of crystalline deposits. It is produced in large amounts as a by-product in the manufacture of hydrochloric acid and nitric acid. It finds commercial use in the manufacture of soda, glass, paper, rayon, dyes, and soap.

Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, is prepared by allowing sodium sulfate to crystallize from a water solution of the salt. It is used in mordanting cloth which is to be dyed and in medicinal remedies.

Sodium nitrate. This salt is often called "Chile saltpeter," because large deposits of the salt are found in northern Chile. They are scattered over an area 200 miles long, and, in places, 40 miles wide. Sodium nitrate is used as a fertilizer and as a source of other nitrates.

Sodium hydroxide. NaOH , known also as *caustic soda*, is one of the most useful compounds of sodium. It is formed when sodium reacts with water. In most reactions involving sodium hydroxide the oxygen and hydrogen atoms remain combined during the change, and for this reason the OH group is called a radical. *Hydroxides* or *bases* are compounds of the hydroxyl radical, OH , with metallic atoms or with groups of atoms that have some metallic properties.

All bases, or hydroxides, have some properties in common. The properties by which we distinguish bases are as follows:

1. They turn moist litmus paper blue.
2. They neutralize acids.
3. They have a slippery feeling.
4. They taste soapy (alkaline).

Properties of sodium hydroxide. Sodium hydroxide is a white solid which usually appears on the market in the form of sticks or pellets. It is deliquescent, having the ability to absorb enough water from the atmosphere to dissolve itself, and it should, therefore, be kept in tightly closed containers. It is very soluble in water, and a large amount of heat is generated when it dissolves.

Sodium hydroxide, like other hydroxides, reacts with acids to form water. With hydrochloric acid, for example, it yields water and a solution of sodium chloride. The replaceable hydrogen of the acid combines with the hydroxyl radical of the base to form water:



A solution of sodium hydroxide attacks animal and vegetable tissue, and for this reason it is known as a caustic. It dissolves silk and wool readily, but cotton is attacked only slightly by a dilute solution of the base. This is the basis of a test to determine the amount of cotton present in a fabric. The fabric is immersed in a warm dilute solution of sodium hydroxide. Silk and wool dissolve in this reagent and cotton remains practically unattacked. With animal and vegetable fats, sodium hydroxide forms soaps.

A solution of sodium hydroxide absorbs carbon dioxide from the air, reacting with it to form a solution of sodium carbonate:



Ordinary *lye* contains sodium hydroxide mixed with sodium carbonate.

Preparation. Much of the sodium hydroxide manufactured today is made by the electrolysis of solutions of sodium chloride. The method will be described later in connection with the preparation of chlorine.

Sodium hydroxide is made on a large scale also by the reaction between sodium carbonate and calcium hydroxide:



The insoluble calcium carbonate precipitates, and the sodium hydroxide is left in solution. It is obtained in the dry state by evaporation of the water.

Uses. Approximately 100,000 tons of sodium hydroxide are used annually in this country in the manufacture of soap. About the same quantity is used in the purification of petroleum products, and nearly as much is used in the manufacture of artificial silk. The textile and paper industries use large amounts of this base. It is used also in the manufacture of many chemicals. In all,

almost a million tons of sodium hydroxide are used annually in the United States.

Questions and Exercises

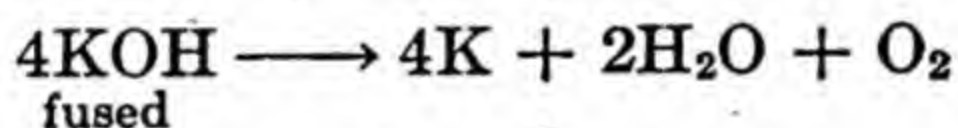
1. Describe the properties of the metal sodium.
2. Why is sodium not found in the free state?
3. How many protons and electrons are there in a sodium atom?
4. What is the atomic weight of sodium?
5. Describe the commercial method for preparing sodium.
6. What are the products formed when sodium reacts with water?
7. What is formed when sodium burns in air?
8. What is a hydroxide? What are the properties of a solution of a soluble hydroxide?
9. Is sodium hydroxide very soluble in water?
10. What products are formed when hydroxides react with acids?
11. Why is sodium not prepared by the electrolysis of a solution of sodium hydroxide in water?
12. What properties are common to most metals?
13. Does water contain replaceable hydrogen?
14. Which of the following substances are malleable? Which are ductile?
(a) paper, (b) copper, (c) cement, (d) iron, (e) gold, (f) glass.
15. Enumerate four uses of sodium hydroxide.
16. Calculate the percentage composition of sodium hydroxide.
17. What weight of hydrochloric acid would react with 400 g. of sodium hydroxide?
18. How could you distinguish a fabric that is all wool from one that is a mixture of wool and cotton? How could you determine the per cent of wool in a fabric containing both wool and cotton?
19. Describe a method of preparing sodium.
20. How many pounds of sodium hydroxide could be prepared by the electrolysis of 1 ton of sodium chloride? How many pounds of chlorine would be produced simultaneously?

PART 2

Potassium, Lithium, Rubidium, and Cesium

Potassium: occurrence and preparation. Potassium, like sodium, is an active metal which is never found free in nature. It is always found in the form of compounds. The salts of potassium are similar to those of sodium. Potassium chloride exists in ocean water, but to a far less extent than does sodium chloride. There is about $\frac{1}{35}$ as much potassium chloride as sodium chloride in sea water. Potassium chloride is found in large deposits in Stassfurt, Germany, in the mineral carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

Potassium is prepared by the electrolysis of its hydroxide, exactly as sodium is prepared by electrolysis of sodium hydroxide. The reaction is expressed by the equation



Hydrogen is liberated at the same time, as explained in connection with the preparation of sodium (see page 166).

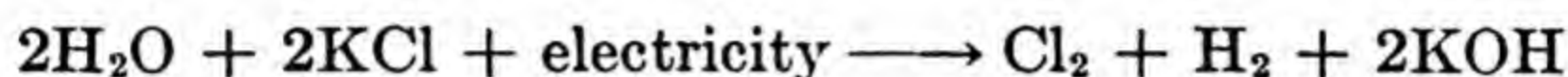
Properties of potassium. Potassium has a silvery white color, but with a slightly bluish tinge. It is softer and less dense than sodium, and it melts at a lower temperature. The chemical properties of potassium closely resemble those of sodium, but potassium is more active. It reacts with water as does sodium, replacing one hydrogen atom from each water molecule, forming hydrogen and the base potassium hydroxide. The reaction is represented by the equation:



The energy liberated is sufficient to set fire to the hydrogen. Potassium and its compounds, when burned on a platinum wire in the flame of a Bunsen burner, impart a violet color to the flame. A trace of any sodium compound obscures the potassium flame; hence cobalt glass should be interposed between the flame and the eye when testing for potassium compounds. The blue glass absorbs the yellow light caused by the sodium and permits the violet light of the potassium flame to pass through.

Potassium nitrate, generally called saltpeter, is used in making gunpowder.

Potassium hydroxide. KOH is formed by methods similar to those for preparing sodium hydroxide. It is one of the important bases used in the laboratory. The equation for its preparation by the electrolysis of a solution of potassium chloride is as follows:



Potassium salts are essential to the growth of plants, and in many places these salts are found in the soil in quantities insufficient for normal development of plant life. These must be supplied to the soil if vigorous crops are desired. Successful methods have been developed for getting potassium compounds from such sources as salt lakes, the fumes from cement kilns, plant ashes, sugar-beet molasses, and the kelp beds of the ocean. Searles Lake, in California, and Carlsbad, in New Mexico, are important sources of potassium compounds.

Lithium, rubidium, and cesium. These alkali metals resemble sodium and potassium in most respects. They have the same silvery metallic luster when first cut, but rubidium and cesium are so reactive that when exposed to the air they ignite spontaneously and burn. In the laboratory all the alkali metals are kept under kerosene to protect them from the oxygen and water vapor present in the air.

Lithium, rubidium, and cesium are prepared by the electrolysis of the fused hydroxides in the same way that sodium is prepared.

The reaction of either of these metals with water is similar to that of sodium and potassium, except that rubidium and cesium decompose water with explosive violence. Hydrogen and the corresponding hydroxides are formed:



These elements react with chlorine as do sodium and potassium, giving the corresponding chlorides. Lithium and its salts impart a deep red color to a flame. Rubidium imparts a violet color to the flame, similar to the color given by potassium.

Questions and Exercises

1. Name the elements that constitute the first main group of the periodic system.
2. Which of these metals is the most abundant in nature?

3. Are these metals found in the free state or in the form of compounds? Give a reason for this condition.

4. What is the valence of each element in the first group of the periodic system?

5. Outline a method for obtaining an alkali metal in the free state.

6. How do the alkali metals behave when placed in water?

7. Explain why sodium sulfate and sodium nitrate impart the same color to a flame.

8. Calculate the weight of hydrogen that can be obtained by the action of 46 g. of sodium on water.

9. Cesium may be made by heating a mixture of metallic calcium and cesium chloride. The volatile cesium is driven out of the mixture by heat. Write the equation for the reaction. Why is it necessary to exclude air when this reaction is carried out?

10. Write balanced equations for the reaction of lithium, potassium, rubidium, and cesium with chlorine.

11. Why are the alkali metals kept in kerosene rather than in water?

12. How many grams of oxygen are formed by the electrolysis of 100 g. of (a) lithium hydroxide, (b) sodium hydroxide, (c) potassium hydroxide, (d) rubidium hydroxide, (e) cesium hydroxide?

PART 3

The Photoelectric Effect; Spectrum Analysis

The atoms of metals do not hold their valence electrons tightly, and in the solid state some of the valence electrons are free to move within the metal. When the metal is heated, some of these free electrons actually escape from the surface of the metal. Electrons may be removed from metals also by the action of light. When light strikes the surface of a metal, electrons are ejected. All metals respond to ultraviolet radiation in this way. The phenomenon is known as the *photoelectric effect*. Not all metals show this effect to the same extent, for it is more difficult to remove electrons from some metals than from others. Electrons are removed from the alkali metals by exposure to ordinary visible light. Most other metals require the action of ultraviolet light. Cesium is the most sensitive photoelectric metal known, and it is commonly used in photoelectric cells. A *photoelectric cell*, or photocell, as it is sometimes called, makes possible most of our talking motion pictures and television. A few years ago cesium was one of the least useful of the metals. It was considered an unimportant chemical curiosity. On account of its photoelectric properties it has since become a very useful and valuable element.

Spectrum Analysis

Attractive neon signs are familiar objects on all electrically lighted streets. The letters or characters in these signs are made of units of sealed bent glass tubing, each unit containing a little neon gas. Metal electrodes are sealed into each unit, as shown in Fig. 107.

The electrodes are connected to a high-voltage source of electricity, and this sends electrons at high velocities from one end of the tube to the other. When a neon atom is struck by a swiftly moving electron, energy is imparted to the atom. This energy which the atom acquires by colliding with an electron is then emitted as light. If we look at this red light through a spectroscope, we see a group of red, orange, and yellow lines, the red lines being most conspicuous.

A spectroscope is an instrument which separates the different kinds of light that come from any source. The light to be analyzed passes through a slit in the instrument, and by means of lenses these entering rays are rendered parallel. The light then passes

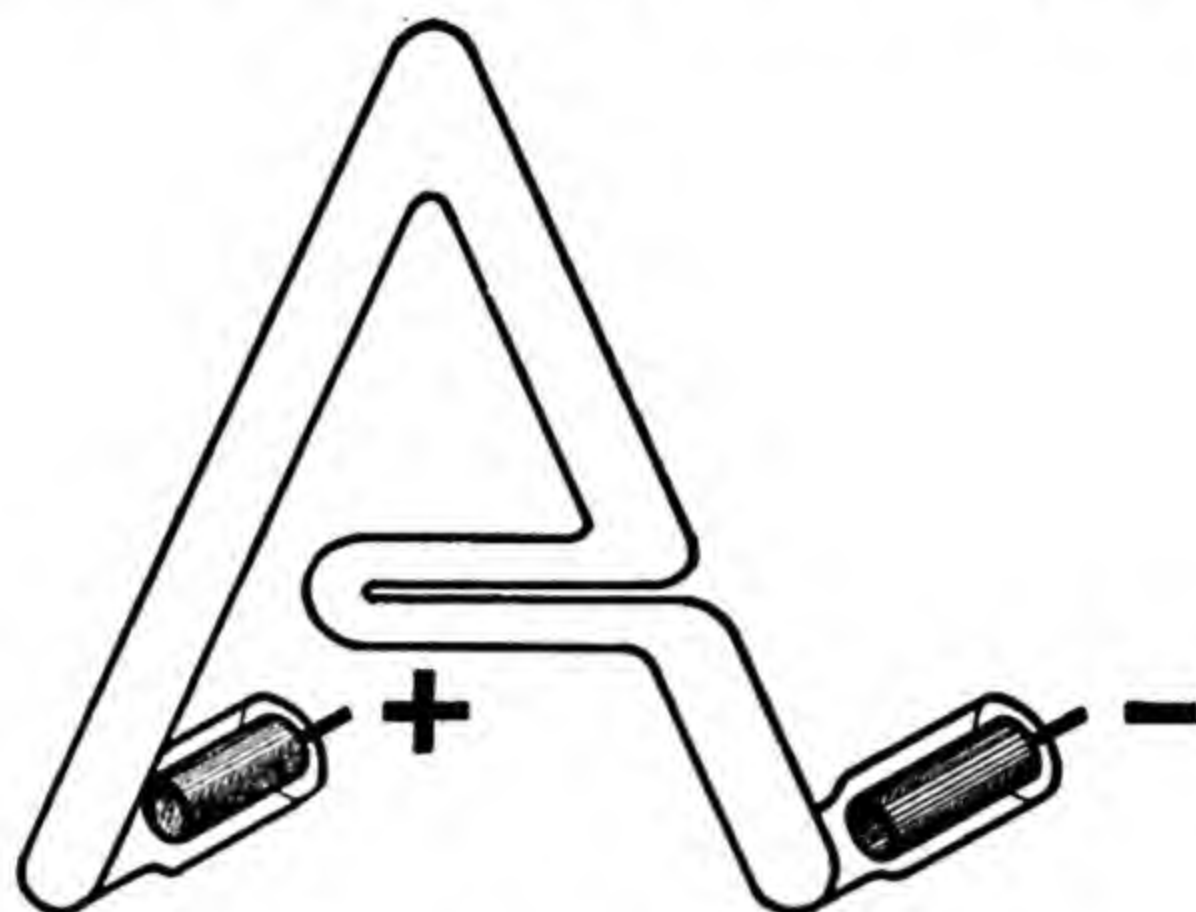


Fig. 107. A neon sign.

through a glass prism, by which it is broken up into its component rays, each of which is colored. Rays that the eye cannot see may be present also. These fall in the ultraviolet and in the infrared regions. Light may be thought of as pulsations or waves in space,



Courtesy, Fisher Scientific Co.

Fig. 108. A spectroscope.

and the frequency of these pulsations determines its color. As the frequency increases, the color changes from red to orange, yellow, green, blue, and violet. Ultraviolet light is radiation of greater frequency than that which produces violet light. We cannot

see ultraviolet light, nor can we see infrared light, which is of lower frequency than red light.

Looking at the neon sign through a spectroscope, we see a group of colored lines near the red end of the spectrum. When hydrogen is substituted for neon gas in such a tube, and the emitted light is viewed through a spectroscope, a different set of lines appears. The bombardment of hydrogen molecules by electrons results in the breaking of some of the molecules into separate atoms. As in the case of neon, these atoms acquire energy from swiftly moving electrons and almost immediately give up the energy in the form of light. The light from hydrogen atoms, however, corresponds to colors quite different from those produced by neon. The frequencies of the pulsations emitted

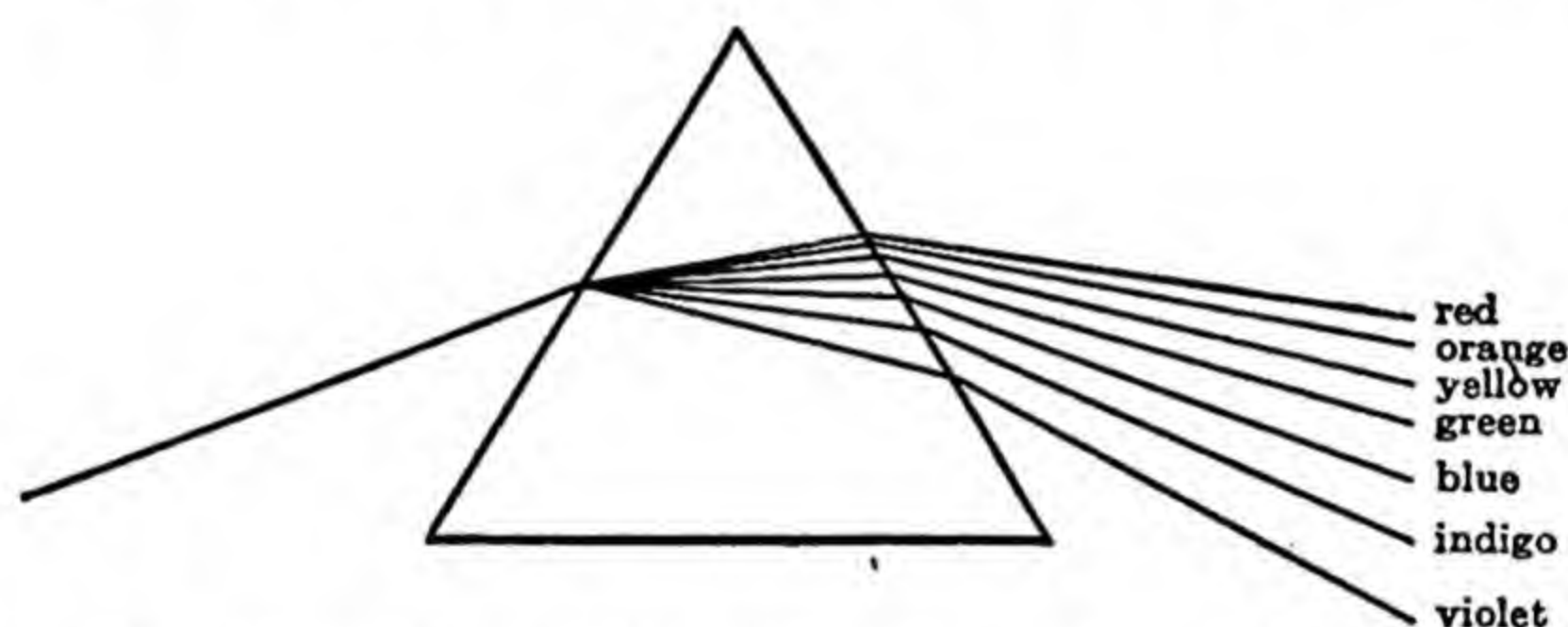


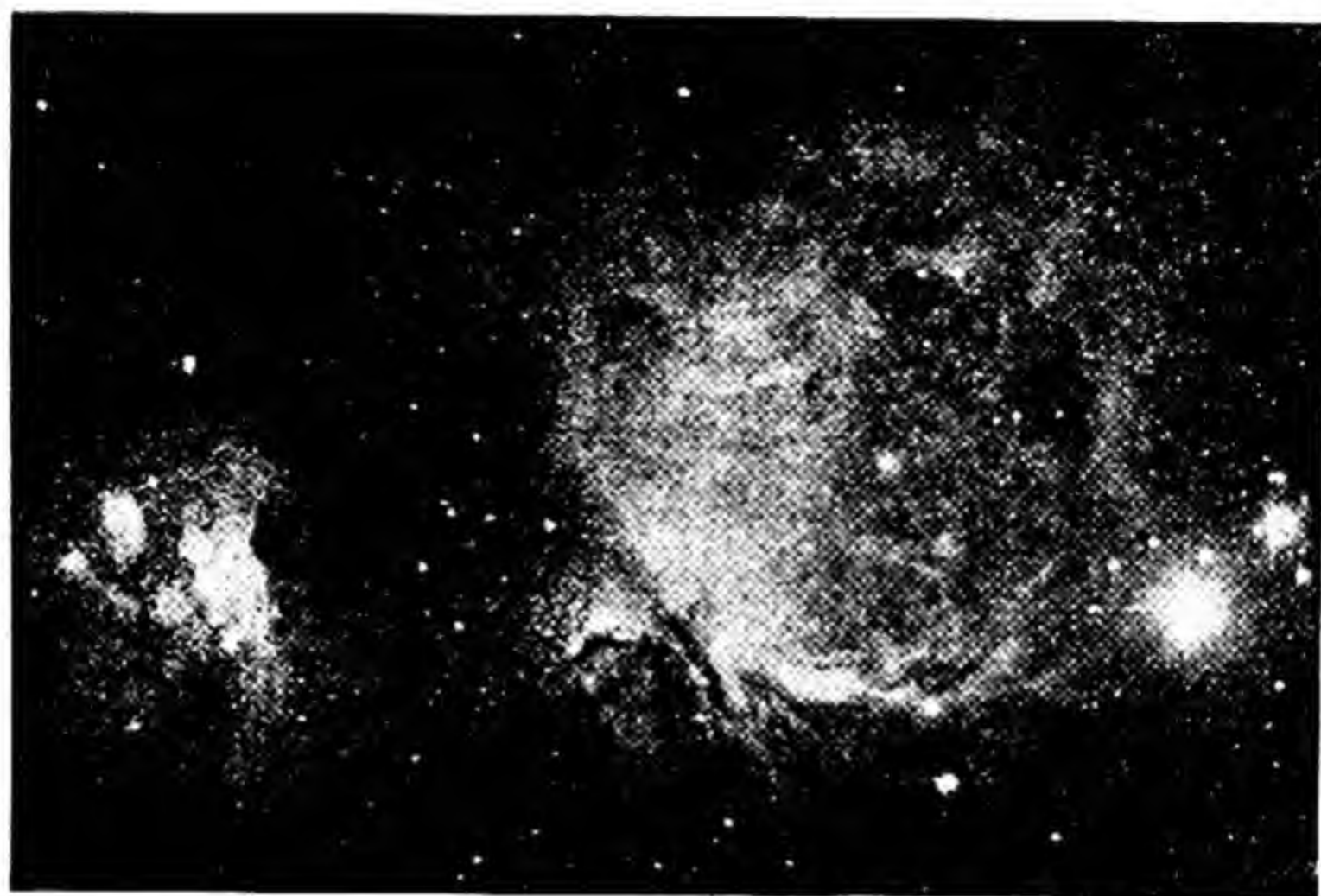
Fig. 109. When a beam of ordinary white light is passed through a triangular glass prism, a spectrum (with all the colors of a rainbow) is formed.

from a hydrogen atom are different from those coming from a neon atom, and the lines fall in different positions in the spectroscope.

Each element shows a characteristic group of lines, and this principle is often used in detecting the presence of any element in an unknown mixture. Flames also show these lines. Common salt held in the flame of a Bunsen burner imparts a yellow color to the flame. The yellow flame, when viewed through a spectroscope, shows two yellow lines so close together that unless a very powerful spectroscope is used they appear as one line. These yellow lines are characteristic of sodium. In the flame the sodium atoms acquire the energy necessary for radiation of light, not so much by electron impacts as by collisions with rapidly moving molecules and atoms in the flame and by the chemical energy set free in the burning process. Potassium and rubidium salts both impart a violet color to the flame, and the potassium and rubidium flames are so similar that it would not be easy to distinguish them by observing the colors. The distinction can be made easily with the aid of a spectroscope, for the spectral lines due to rubidium

and those due to potassium are in different positions in the spectrum.

It was by means of the spectroscope that cesium and rubidium were discovered. In 1860 Bunsen and Kirchhoff, two German chemists, were analyzing the salts found in certain mineral waters. After separating most of the ordinary salts by the process of evaporation and crystallization, they examined the residue by vaporizing it in a flame and observing the lines that appeared in the spectrum of the flame. They discovered lines that could not be duplicated by any known elements. In order to obtain



Courtesy, Lick Observatory

Fig. 110. The great nebula of Orion.

samples of the salts of these new elements for analysis, they evaporated 44 tons of the water, and from this great quantity of water they obtained 13 g. (less than $\frac{1}{2}$ oz.) of the salts of cesium and rubidium. A paragraph from their report on cesium is reproduced here:

“As no other elementary body produces two blue lines in this position of the spectrum we may consider that the existence of this hitherto unknown alkaline element was thus placed beyond doubt. The facility with which a few thousandths of a milligram of this body may be recognized by the bright blue light of its incandescent vapor, even when mixed with large quantities of more common alkalies, has induced us to propose for it the name cesium (and the symbol Cs), derived from the Latin *caesius*, used to designate the blue of the clear sky.”

In a similar way rubidium was discovered. The name for this element was derived from the Latin *rubidus*, which was used to denote the darkest red color. The most characteristic spectral lines of rubidium are in the dark red portion of the spectrum.

With the aid of the spectroscope, the element helium was detected in the sun before it was known on the earth. Its name is derived from *helios*, the Greek word for the sun.

The spectroscope has revealed to us the composition of stars and nebulae. A picture of the gaseous nebula of Orion is shown in Fig. 110 and a photograph of its spectrum is reproduced here. This spectrum tells us with certainty that the nebula of Orion contains the gases hydrogen, helium, nitrogen, and oxygen. Not only can the composition of the stars be determined by the spectroscope, but their temperatures can also be estimated. Some lines



Fig. 111. Spectrum of Orion.

appear in the spectrum only when the light comes from extremely hot bodies; other lines appear when the source of light is at a relatively low temperature.

Questions and Exercises

1. Do all metals give off electrons when heated to incandescence?
2. Do all metals lose electrons when light shines on them?
3. Which element yields electrons most readily? What practical use is made of this element on account of its tendency to give up electrons when ordinary light strikes it?
4. Raindrops are capable of separating the rays of different frequencies in sunlight. Have you seen a spectrum produced in this way? What name is given to this spectrum?
5. A small mirror having a beveled edge acts as a prism and may be used to separate rays corresponding to different frequencies. Have you seen a spectrum produced in this way?
6. How was helium discovered?
7. How was cesium discovered?
8. Does a cold gas produce a spectrum?
9. How could you distinguish sodium chloride from rubidium chloride?
10. Why is neon used in electric lamps and in electric signs?

UNIT VI

Group VII of the Periodic Table: the Halogens and Halogen Acids

PART 1

Chlorine

We have studied sodium, the metallic part of sodium chloride, and the other members of the sodium family. Let us now turn our attention to the nonmetallic part of common salt; that is, to chlorine.

If we examine the Periodic Table, we find that chlorine is in the seventh vertical column. It is a member of a group of closely related elements consisting of fluorine, chlorine, bromine, and iodine. These elements (members of Group VII) are called *halogens*, from the Greek word which means "salt-producing." The name was given to these elements because chlorine was found in common table salt. Compounds of the halogens with all the metals in Group I closely resemble sodium chloride, and they are all salts. The halogens have seven electrons in their valence orbits, and each has a tendency to acquire one additional electron. Hence, these elements are all monovalent and they react readily with hydrogen, forming compounds with the formulas HF, HCl, HBr, and HI, respectively. They react also with the metals in Group I, forming some of the type NaCl, KCl, LiBr, and RbF. They unite also with the metals in Groups II and III. Metals are elements which readily give up electrons, and they occur, in general, on the left side of the Periodic Table. The nonmetals acquire electrons and they are on the right side of the table.

The halogens also form compounds in which they share electrons with other elements (see Part 5). In these compounds, the halogens have valences ranging from one to seven.

At ordinary temperatures fluorine and chlorine are gases, bromine is a liquid, and iodine a solid. Bromine and iodine are easily vaporized, and chlorine is easily liquefied. In the gaseous state all these elements are diatomic; that is, each molecule consists of two atoms, and their formulas are: F_2 , Cl_2 , Br_2 , and I_2 .

These formulas are used to represent the halogens, whether they are in the solid, liquid, or gaseous state.

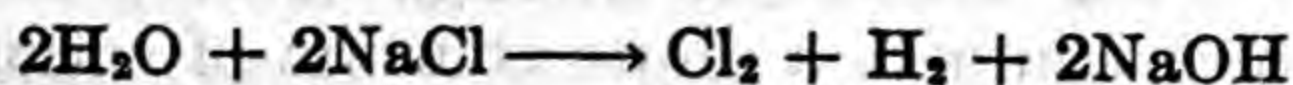
The following table of the physical properties of the halogens shows the regular trends in these properties as we pass from the one of lowest atomic number to the one having the highest atomic number.

PHYSICAL PROPERTIES OF THE HALOGENS

	Fluorine	Chlorine	Bromine	Iodine
Symbol.....	F	Cl	Br	I
Melting point, °C.....	-223	-102.1	-7.3	113
Boiling point, °C.....	-188.3	-34.7	58.0	183
Color of gas.....	Light yellow	Greenish yellow	Reddish brown	Violet
Atomic weight.....	19.0	35.46	79.92	126.92
Isotopes.....	19	35, 37	79, 81	127
Atomic number.....	9	17	35	53
Electron structures:				
1st shell.....	2	2	2	2
2nd shell.....	7	8	8	8
3rd shell.....	—	7	18	18
4th shell.....	—	—	7	18
5th shell.....	—	—	—	7

Chlorine, the commonest and best known of these elements, is never found in nature in the free state. The most abundant compound of chlorine is sodium chloride. Chlorine was first obtained by Scheele in 1774 by a method still commonly used in the laboratory. Not until 40 years later was it definitely shown by Davy that chlorine is really an element.

Preparation. If we wish to make chlorine on a large scale, we should naturally prepare it from sodium chloride, its cheapest and most widely distributed compound. It is actually prepared commercially by the electrolysis of brine—a solution of sodium chloride. When an electric current is passed through a salt solution, chlorine is evolved at the positive electrode and hydrogen at the negative electrode. The chlorine comes from the salt, and the hydrogen from the water. Since sodium chloride and water are both decomposed, the reaction is somewhat complicated. The following equation for the total change shows us the substances that are used and the new substances that are formed, with the proportions of each entering into the reaction when a solution of sodium chloride is electrolyzed:



For each molecule of chlorine liberated, two molecules of water and two molecules of sodium chloride must disappear. At the same time, one molecule of hydrogen and two molecules of sodium hydroxide are formed.

In a more convenient laboratory method for the preparation of chlorine, hydrochloric acid is used as a source of chlorine. An electric current is passed through a concentrated solution of

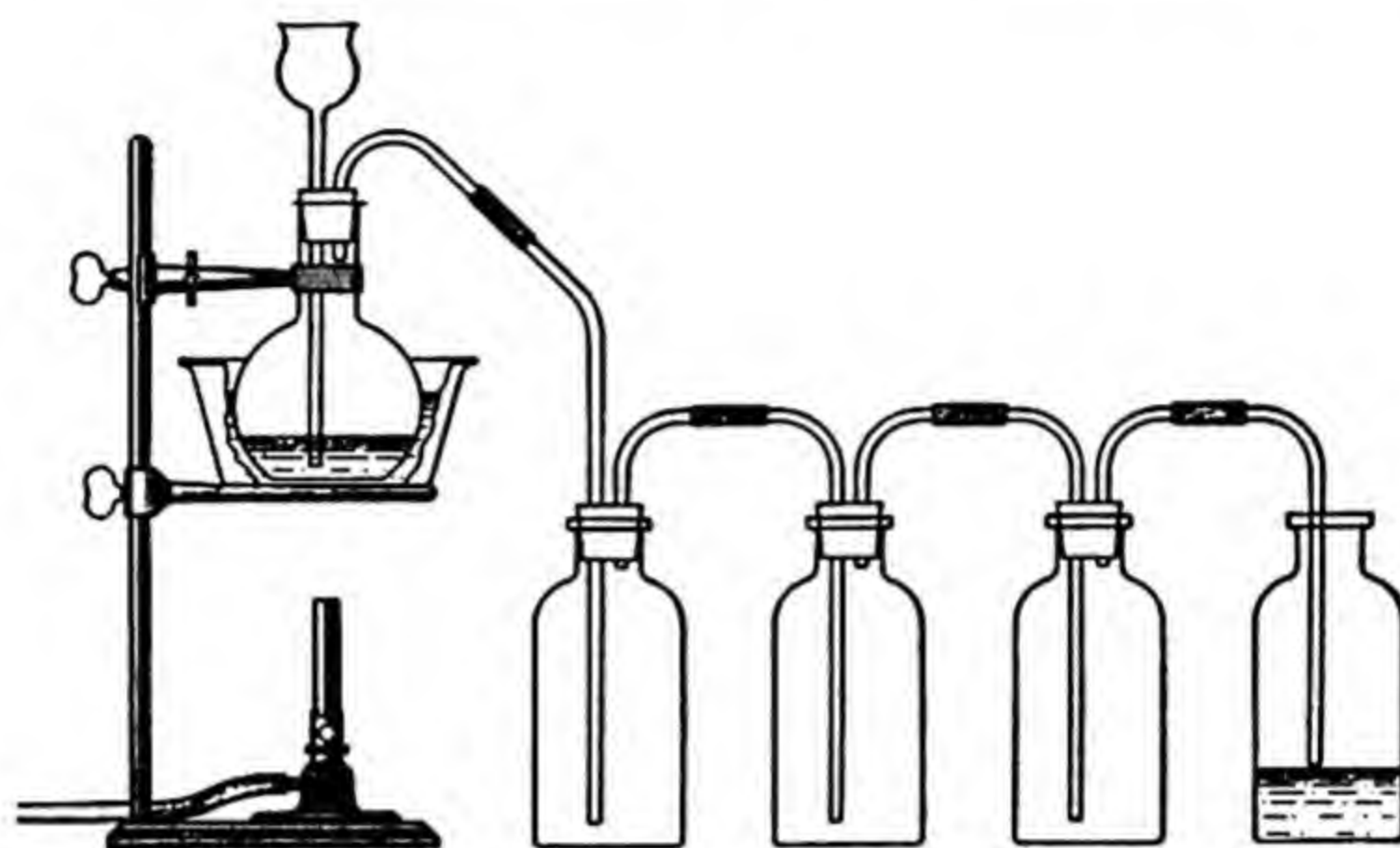
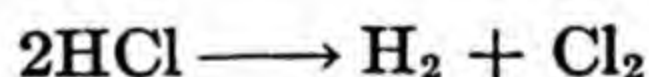
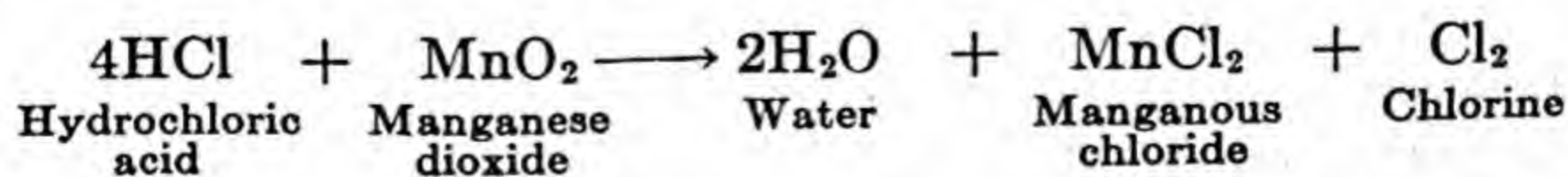


Fig. 112. A laboratory method of preparing chlorine.

hydrochloric acid in an apparatus similar to that which is used for the electrolysis of water. The acid is separated into two elements, hydrogen and chlorine:



The usual laboratory method depends upon the use of an oxidizing agent to remove the hydrogen from the HCl molecule, leaving the chlorine free. The oxidizing agent usually employed is manganese dioxide. Solid manganese dioxide is mixed with a solution of hydrochloric acid, and when heated, this mixture yields chlorine, water, and manganese chloride.



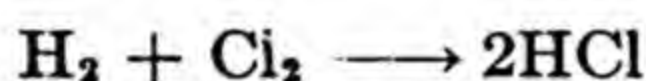
In this reaction, a mixture of sulfuric acid and sodium chloride may be substituted for hydrochloric acid.

The chlorine is usually collected by the displacement of air as shown in Fig. 112. Chlorine is much heavier than air. The heavy chlorine remains in the bottles attached to the generator, the lighter air being forced out through the top and over to the last bottle, which contains a dilute solution of sodium hydroxide.

The purpose of the sodium hydroxide solution is to absorb any chlorine gas which escapes from the first bottle. This prevents the poisonous gas from getting into the air of the laboratory.

Properties. Chlorine is a greenish yellow gas which is quite soluble in water. It has a penetrating odor and produces a suffocating effect when breathed. In extremely small concentrations (a few hundred cubic centimeters mixed with the air in a large room) chlorine has been used as a remedy for colds. In larger concentrations this effect is reversed and the disorder is aggravated. Symptoms of a cold may be artificially produced by the injurious action of chlorine on the membranes of the throat, bronchial tubes, and lungs. At high concentrations, chlorine is a poisonous gas.

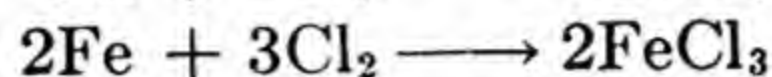
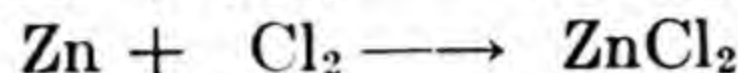
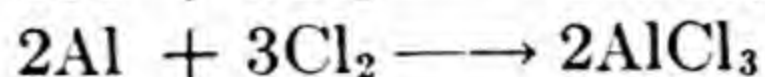
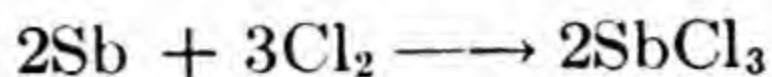
When cooled to -33.8°C . at atmospheric pressure, chlorine condenses to the liquid state, and under high pressure it is a liquid at ordinary temperatures. Liquid chlorine is transported in sealed steel cylinders or in tank cars. A jet of chlorine will burn in an atmosphere of hydrogen, or a jet of hydrogen will burn in an atmosphere of chlorine. In this process of combustion, hydrogen and chlorine combine to form hydrogen chloride according to the equation:



At room temperature, and in the dark, chlorine and hydrogen combine very slowly, but if the temperature of the mixture is raised or if light is allowed to shine on the mixture, the reaction proceeds faster. At a high temperature, hydrogen and chlorine combine explosively, and at ordinary temperatures a mixture of the two gases explodes when exposed to strong sunlight. There are many reactions that proceed only in light or that proceed faster in light than in the dark. Such processes are known as *photochemical* reactions. Many of the changes occurring in growing plants are reactions of this kind.

Chlorine reacts with many metals. Powdered antimony, for example, ignites when dropped into a jar containing chlorine, and the powder sparkles as it combines with the chlorine vapor, forming antimony chloride, SbCl_3 . Aluminum, zinc, iron, and many other metals burn readily in an atmosphere of chlorine. Chlorine resembles oxygen in this respect. Although chlorine and oxygen belong to different families of elements, the two show marked similarities in reactions with hydrogen and the metals. Chlorine, like oxygen, may be looked upon as a supporter of combustion. Chlorine, however, does not combine directly with carbon, as does oxygen.

The reactions of chlorine with various metals are represented by the following equations:



Chlorine is a good bleaching agent. A piece of colored cloth, if moistened with water and dropped into chlorine gas, becomes colorless, or at least lighter in color, within a short time. Many

colored substances are affected by chlorine in this way. Chlorine is used to bleach cotton, linen, and wood pulp. It cannot be used on silk or on wool, for it destroys these textile fibers. Even cotton fibers become disintegrated if subjected for a long time to the action of moist chlorine.

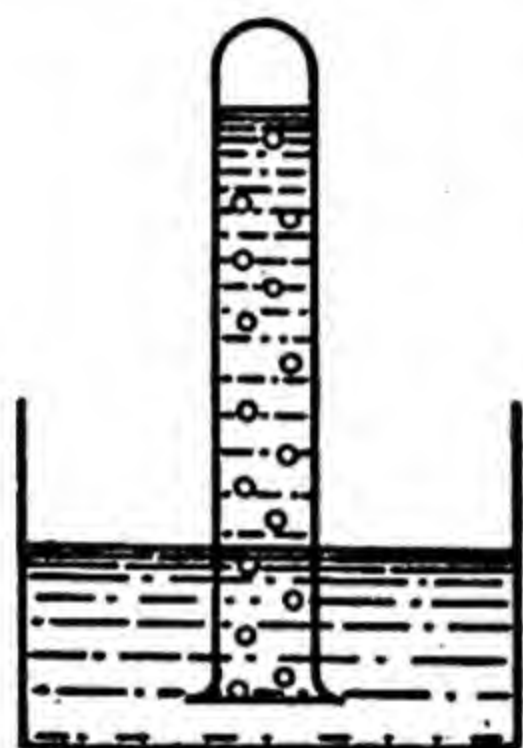
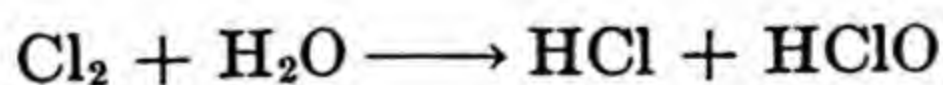


Fig. 113. Chlorine liberates oxygen from water.

The great tendency of chlorine to decompose hydrogen compounds may be illustrated by dropping a small piece of paper or cloth, moistened with turpentine, into a jar of chlorine gas. The turpentine, which is composed of carbon and hydrogen, immediately ignites and burns in the chlorine. The carbon in the turpentine is set

free, and a dense cloud composed of fine particles of carbon may be seen rising from the jar. A wax candle also burns in chlorine, the hydrogen of the wax combining with the chlorine. The carbon of the wax does not combine with the chlorine, and a dense black smoke is produced.

Chlorine reacts slowly with water, forming hypochlorous acid, HClO , and hydrochloric acid, HCl :

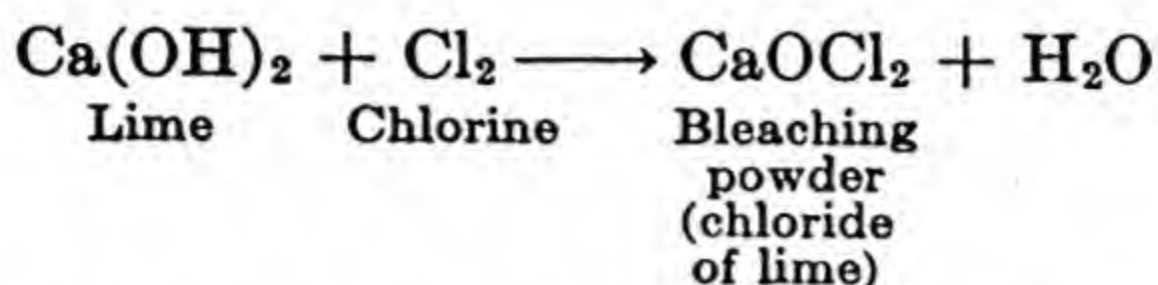


If the solution is allowed to stand, especially in sunlight, the hypochlorous acid decomposes, yielding oxygen and hydrochloric acid. The reaction between chlorine and water in bright light may be represented by the equation:

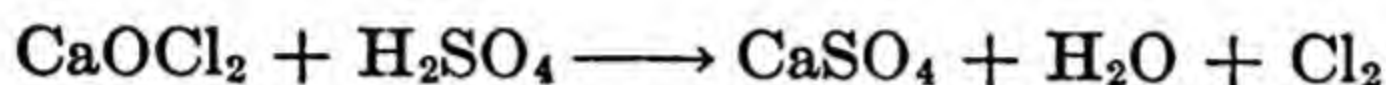


The reaction may be demonstrated by exposing to sunlight an inverted tube containing water in which chlorine is dissolved. In a short time bubbles of oxygen may be seen rising in the tube.

Bleaching powder is made by allowing slaked lime to absorb chlorine:

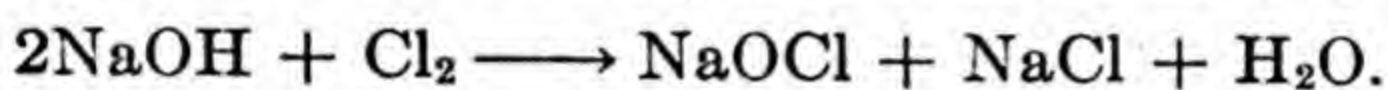


The chlorine is released from the powder by treatment with any dilute acid:



Since chlorine is readily released from bleaching powder, the lime may be regarded as a convenient carrier of chlorine. Cotton is commonly bleached by immersing it first in a mixture of bleaching powder and water and then in a dilute solution of an acid.

Sodium hydroxide solution absorbs chlorine, forming a solution of sodium hypochlorite, NaOCl, and sodium chloride:



Sodium hypochlorite, like chloride of lime, is a bleaching agent. Bleaching solutions made by this reaction appear on the market under various trade names.

Uses. Chlorine is used as a disinfectant. Most public drinking waters are treated with small amounts of chlorine, which in gaseous form is usually fed slowly from tanks of liquid chlorine into the water supply. The chlorine remains in the water long enough to destroy bacteria, but it gradually reacts with the water and is converted into hydrogen chloride, which in turn forms salts called chlorides. By the time the water reaches the consumer, practically all the chlorine has been converted into chlorides, which are harmless, and the amounts of these salts in drinking water are usually so small as to escape detection by taste.

A solution of chlorine in water also forms an effective bleaching agent. The action is due to the hypochlorous acid formed between the chlorine and water (see page 184).

Although much chlorine is consumed by the textile industries, the largest application of chlorine is in the bleaching of wood pulp. Chlorine was at one time used extensively in extracting gold from its ores, but this process has been largely replaced by other methods. Phosgene, COCl_2 , and mustard gas, $(\text{C}_2\text{H}_4\text{Cl})_2\text{S}$, are common poisonous compounds which contain chlorine.

Questions and Exercises

1. How is chlorine prepared?
2. Enumerate the uses of chlorine.

3. Is chlorine abundant or rare (a) in the free state? (b) in combination with other elements?

4. Name five metals which will combine with chlorine.

5. What products are formed when a solution of chlorine in water is exposed for a long time to light?

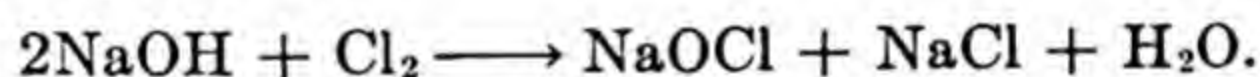
6. When chlorine reacts with aluminum, zinc, and iron, the compounds aluminum chloride (AlCl_3), zinc chloride (ZnCl_2), and iron chloride (FeCl_3), respectively, are produced. Write equations for these reactions.

7. India ink contains finely divided carbon, and blue ink is made from a dye. Which of these inks would you use to mark linen that is to be sent to a commercial laundry? (Chlorine is used in many laundries as a bleaching agent.)

8. Oxygen and hydrogen chloride gas (HCl), when passed over a catalyst at a high temperature, produce chlorine. From a consideration of the formulas of the substances involved, predict what substance besides chlorine is produced. Write an equation for the reaction.

9. Chlorine reacts with ammonia gas, NH_3 , forming nitrogen gas, N_2 , and hydrogen chloride. Write a balanced equation for the reaction.

10. If sodium hydroxide and chlorine each cost 10 cents per kilogram (1000 g.), what is the cost of making a bleaching solution from 500 g. of a 20 per cent solution of sodium hydroxide?



11. Describe two methods for transporting chlorine.

12. Why is chlorine not collected over water as hydrogen and oxygen are?

13. Account for the black smoke formed when a candle burns in chlorine, and the lack of smoke when it burns in oxygen.

14. How many grams of chlorine are formed by the action of manganese dioxide on 292 g. of hydrochloric acid? How many grams of manganese dioxide will be required to oxidize this quantity of acid? How many grams of water will be formed?

15. How many grams of sodium chloride must be electrolyzed to release 710 g. of chlorine? How many grams of hydrogen will be formed at the same time?

PART 2

Fluorine, Bromine, and Iodine

Fluorine

Occurrence and preparation. Fluorine, the first member of the halogen family, is a very reactive gas and difficult to obtain in the free state. It is the most active of the halogens. It combines so readily with other elements that few people have seen it in its pure state. Its most important natural compounds are the minerals *fluorite* (CaF_2), the most useful of all fluorine compounds, and *cryolite* (Na_3AlF_6), which is used in the preparation of aluminum.

If we were to try to make fluorine by a method similar to that for making chlorine—namely, by heating hydrofluoric acid with manganese dioxide—the experiment would be a failure. Oxygen is unable to take hydrogen away from fluorine.

Many early investigators tried to obtain fluorine in the free state, but it was not until 1886 that the isolation of pure fluorine was accomplished. This was done by the French chemist Moissan, who decomposed liquid hydrofluoric acid by passing a current of electricity through it. Potassium fluoride was dissolved in the acid to make it a better conductor of electricity. The apparatus used was a platinum U-tube with electrodes made of the same metal. Hydrogen was produced at the negative electrode and fluorine at the positive electrode. Today fluorine is made by the electrolysis of molten potassium hydrogen fluoride, KHF_2 , and the apparatus is made of copper. The products at the electrodes are hydrogen and fluorine. The total reaction is expressed by the equation:

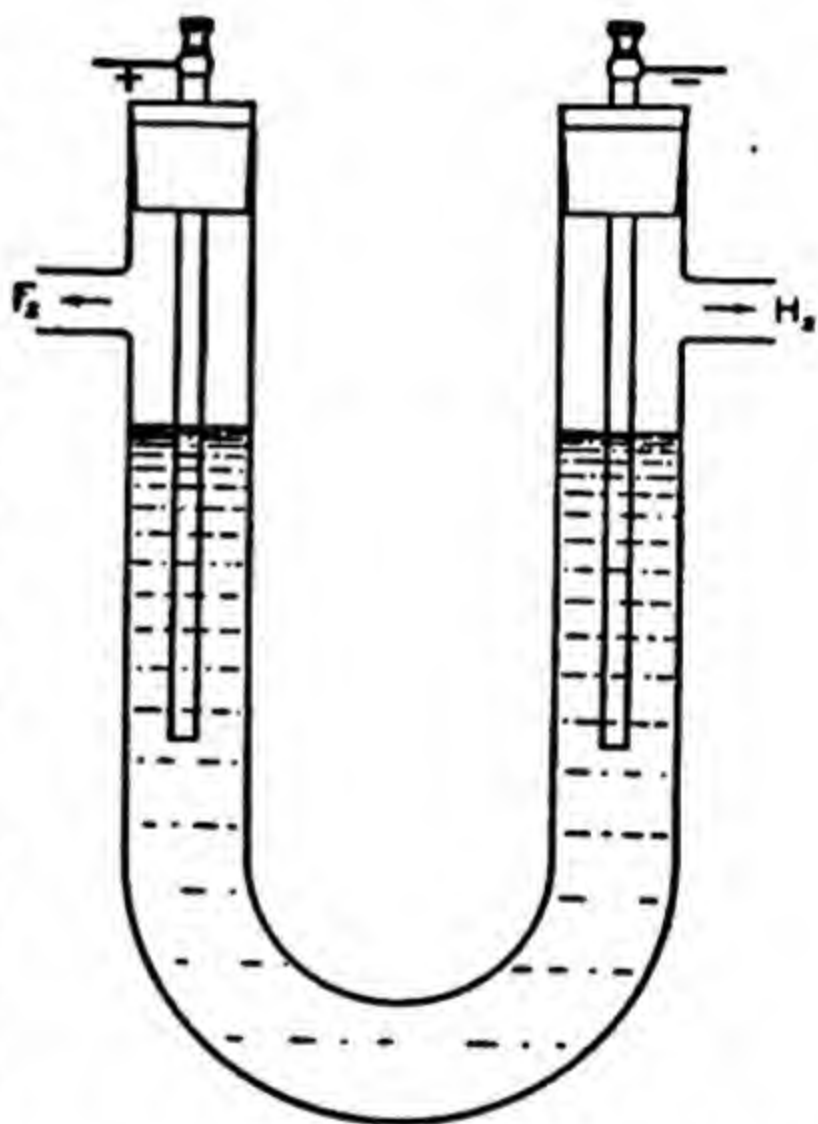


Fig. 114. Preparation of fluorine by electrolysis of hydrofluoric acid.

Free fluorine has no industrial use, but it is sometimes used in the laboratory in the preparation of metallic fluorides.

Properties. At ordinary temperatures fluorine is a light yellow gas. With copper it quickly forms a thin coating of copper fluoride on the surface of the metal, and this coating protects the copper below the layer from further action of the gas. This makes it possible to use a copper vessel in the preparation of fluorine, a fact not known when Moissan constructed his expensive equipment. There are relatively few compounds that fluorine

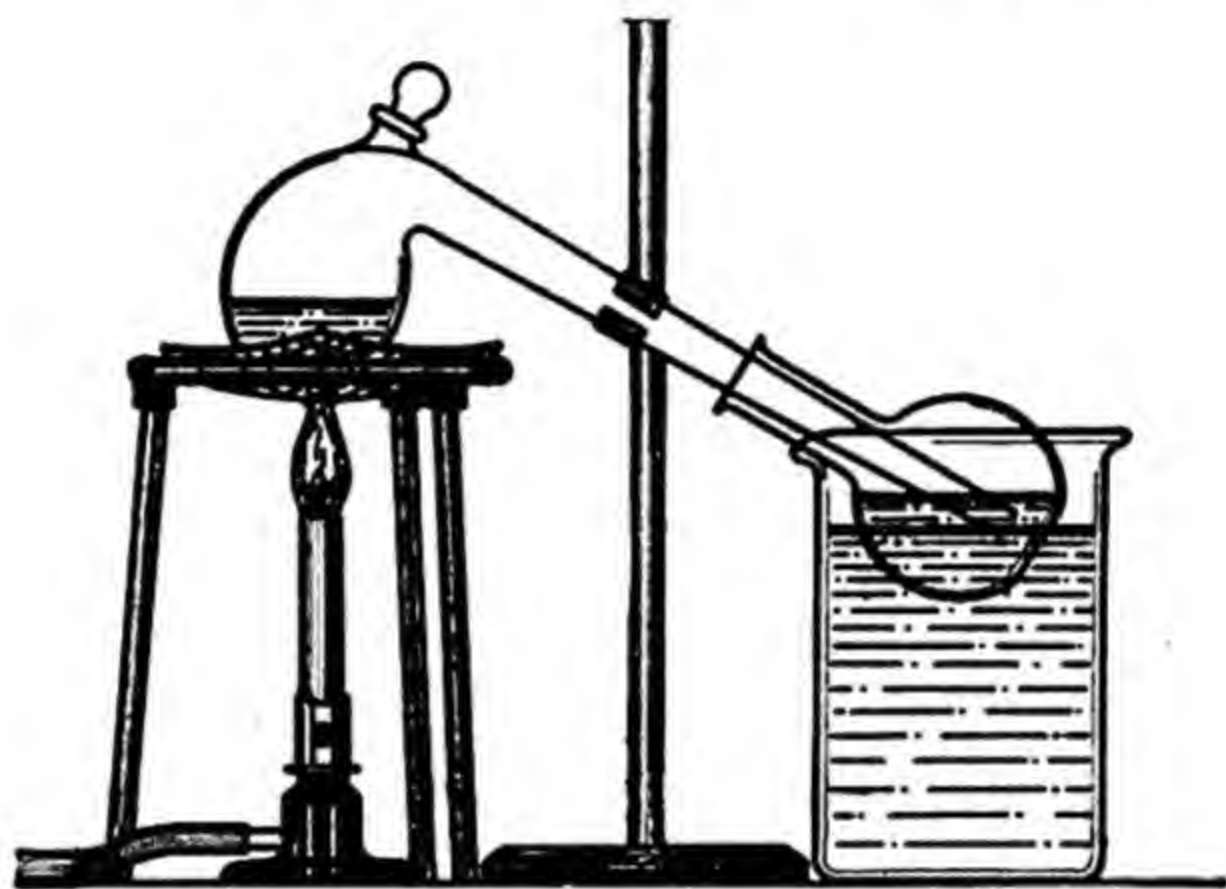


Fig. 115. Preparation of bromine.

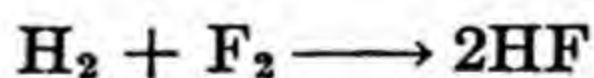
will not attack. It combines with water to form ozone and hydrofluoric acid:



This reaction occurs so rapidly in moist air that it is doubtful whether anyone has ever smelled fluorine. The odors and effects of ozone and of hydrofluoric acid are all that can be detected.

Powdered charcoal, sulfur, iodine, bromine, phosphorus, and almost all the metals react so vigorously with fluorine that they take fire spontaneously in an atmosphere of this gas. Fluorine gas is liquefied at -187°C . at ordinary pressure, and in this state it does not react with glass. At room temperature, the gas slowly decomposes glass.

Fluorine combines rapidly with hydrogen, forming hydrogen fluoride:



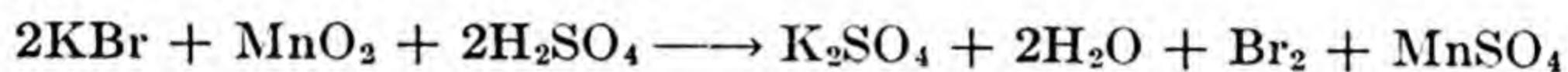
Bromine

Occurrence and preparation. Sea water contains small quantities of bromides mixed with very much larger quantities of chlorides. All salt beds that have been formed from the drying up

of sea water contain bromides, including sodium bromide, potassium bromide, and magnesium bromide. The largest deposit of this kind is in Stassfurt, Germany, and this is one of the principal sources of bromine. Both in Germany and in the United States bromine is recovered from the waste liquor obtained in the process of refining table salt.

Bromine may be prepared in the laboratory in a way similar to that for preparing chlorine: by the action of manganese dioxide on hydrogen bromide (hydrobromic acid). The latter, however, is not very stable, and bromine is prepared, usually, in a slightly different way.

A mixture of sodium bromide (NaBr) or potassium bromide (KBr) is heated with manganese dioxide and hot sulfuric acid. The bromine formed passes out of the mixture in the form of vapor, which condenses to a liquid when cooled. The liquid is usually collected under water:



Compare this process of obtaining bromine with the preparation of chlorine (see page 182).

Properties. At room temperature, bromine is a dark red liquid which boils at 58.0°C . It is a little more than three times as heavy as water. Liquid bromine is kept in a closed bottle, and a considerable amount of bromine gas is present in the space above the liquid. The gas, like the liquid, has a red color. Bromine is sufficiently soluble in water to produce a light reddish-brown solution, similar in color to that of the gas. It is very soluble in chloroform (CHCl_3), carbon tetrachloride (CCl_4), and carbon disulfide (CS_2).

Bromine attacks the mucous membranes and, if inhaled in large quantities, may prove fatal. When accidentally inhaled, its effects may be counteracted to some extent by breathing very dilute ammonia gas, or alcohol vapor. Bromine produces severe burns on the skin. After any accident with bromine, that portion of the skin which has come in contact with the bromine should be washed with carbon tetrachloride or alcohol, and later covered with olive oil.

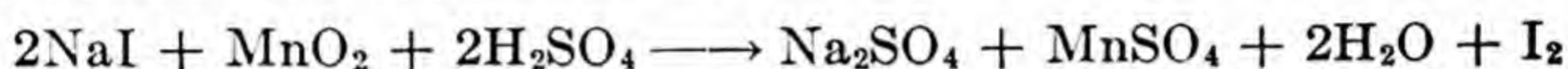
Bromine is similar to fluorine and chlorine in chemical properties, but its reactions are slower. It combines with hydrogen only when heated, whereas chlorine combines with hydrogen at room temperature in the presence of sunlight, and fluorine unites with hydrogen rapidly at low temperatures even in the dark.

Bromine is used in the preparation of most of the bromides. The major portion of the American production of bromine is

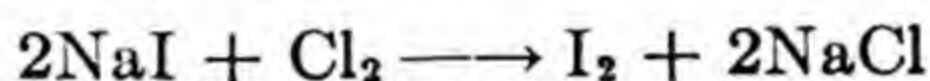
consumed in making lead tetraethyl, the antiknock constituent of ethyl gasoline.

Iodine

Occurrence and preparation. Iodine is not found in nature in the free state. Like the other halogens, it is obtained from compounds. Seaweed, or kelp, has the property of absorbing and using iodides from sea water, and when the kelp is burned iodides are found in the ash. Iodine is obtained from the ash by leaching it with water, concentrating the solution, and then adding manganese dioxide and sulfuric acid:



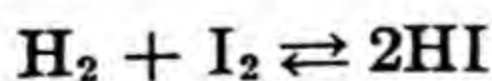
It is liberated also by the action of chlorine on an iodide:



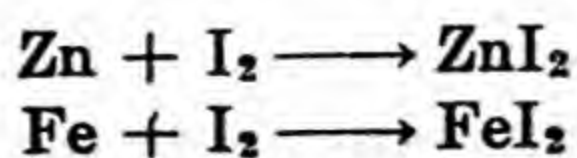
Iodine, in the form of sodium iodate, NaIO_3 , is found with sodium nitrate in the salt deposits of Chile. This is the most important source of iodine.

Properties. At ordinary temperatures iodine is a solid with a brownish gray metallic luster. On heating, it is converted into a violet-colored gas. It is soluble in carbon disulfide, in alcohol, and in a water solution of potassium iodide. It is only slightly soluble in pure water. A solution of iodine in alcohol is known as *tincture of iodine*. Iodine melts at 113°C ., but even below this temperature it passes rapidly into the vapor state, and the vapor recondenses to the solid state without liquefying. This process, called *sublimation*, is the method adopted for the purification of iodine. Any substance that passes from the solid state to the vapor state and recondenses to the solid state without melting, or appearing as a liquid, is said to *sublime*.

Although iodine is similar to chlorine and bromine in its chemical behavior, it reacts in all cases much less vigorously than do these two elements. It combines with hydrogen only at very high temperatures, forming hydrogen iodide, and at high temperatures the reaction is reversible.



It reacts with many metals to form the iodides. Zinc and iron, when heated, react with iodine to form zinc iodide and ferrous iodide, respectively:



Iodine imparts a blue color to cold starch paste. This color reaction provides a good test for free iodine. The paste is prepared by mixing 1 g. of starch with 200 cc. of cold water, heating the mixture to the boiling point, and then allowing it to cool. A small quantity of this preparation (boiled starch in water) is poured into a test tube, and to it is added a small amount of the mixture to be tested. A blue color appears if iodine is present.

Iodine is used in the preparation of iodides and as an antiseptic. Tinctures of iodine and iodoform, CHI_3 , are common antiseptics. In the form of metallic iodides, iodine is used in the prevention and cure of goiter, a disorder of the thyroid gland.

The replacement series of the halogens. Every halogen atom has a tendency to acquire one extra electron to form a halide ion. The order in which the halogens show this affinity for an extra electron is fluorine, chlorine, bromine, and iodine. If chlorine, Cl_2 , is added to a solution containing a bromide (for example, sodium or potassium bromide), the chlorine will rob bromine of the electron which it acquired when it reacted with the metal. Chlorine can do this because it has the greater affinity for electrons. The replacement is usually represented by an equation of the type:



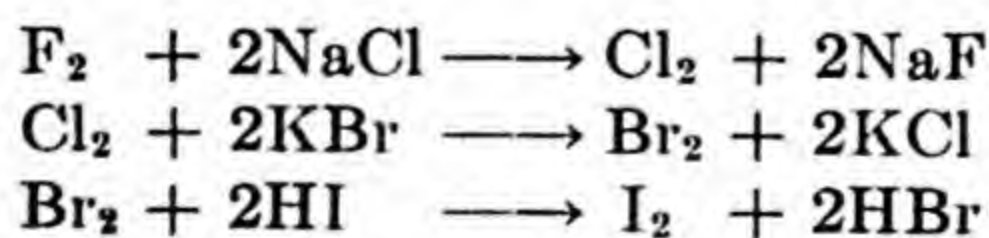
Free bromine is obtained commercially by passing chlorine gas into a solution of a bromide.

Chlorine replaces either bromine or iodine. Bromine replaces iodine from an iodide but not chlorine from a chloride. Fluorine has the greatest tendency of all elements to acquire and hold an additional electron. Fluorine, therefore, can replace chlorine, bromine, or iodine from chlorides, bromides, and iodides, respectively.

If we write the halogens in the order



we may state that any element in this group will liberate any element on the right of it from the corresponding halide. For example:



But



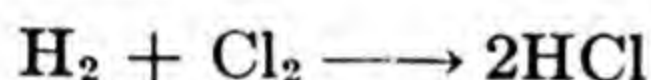
Questions and Exercises

1. What is meant by the term *sublimation*?
2. Name three solvents for bromine and three solvents for iodine.
3. (a) Make a diagram of the apparatus used in the laboratory for the preparation and collection of bromine. (b) Name the chemical materials used and give a reason for the use of each.
4. Name three physical and three chemical properties of bromine.
5. What is a tincture?
6. State the physical and chemical properties of iodine.
7. Name the elements belonging to the halogen family in the order of their increasing activity. Why are they not found free in nature?
8. What would happen if bromine were added to a solution of (a) sodium iodide, (b) hydrogen chloride, (c) potassium fluoride? Write the equations if reactions occur.
9. Write the equation for the reaction, if one takes place, when a solution of chlorine is added to a solution of (a) hydrogen iodide, (b) sodium fluoride, (c) potassium bromide.
10. Write the equation for the reaction, if one occurs, when (a) a solution of fluorine is added to a solution of sodium iodide, (b) a solution of iodine is added to one of sodium fluoride, (c) a solution of fluorine is added to one of sodium chloride.
11. How many grams of bromine can be formed by the action of an excess of sulfuric acid and manganese dioxide on 1.190 g. of potassium bromide?
12. How many grams of H_2SO_4 must be used with MnO_2 and an excess of sodium iodide in order to make 127 g. of iodine?

PART 3

Hydrochloric Acid

Preparation. The most important compound of chlorine, with the exception of sodium chloride, is hydrogen chloride. Hydrogen chloride is a colorless gas which may be produced by the direct combination of hydrogen and chlorine:



This method is so violent and so difficult to control in the laboratory that it is seldom used.

A solution of hydrogen chloride in water is called hydrochloric acid, or "muriatic acid." In the laboratory, and on an industrial scale, hydrochloric acid is made by warming a mixture of common salt and sulfuric acid. The sodium chloride supplies the chlorine part of the molecule, and sulfuric acid is the source of the hydrogen part:



Here is an example of a reaction involving double decomposition. The hydrogen in the sulfuric acid and the sodium in the sodium chloride change partners during the reaction. The apparatus used is shown in Fig. 116. Hydrogen chloride released from the mixture is obtained in the gaseous state in the first bottle and as an aqueous solution in the second bottle. The outlet tube should not touch the water; otherwise water would rise in the tube, since hydrogen chloride is very soluble in water. If water were allowed to run back into the generator, an explosion might result

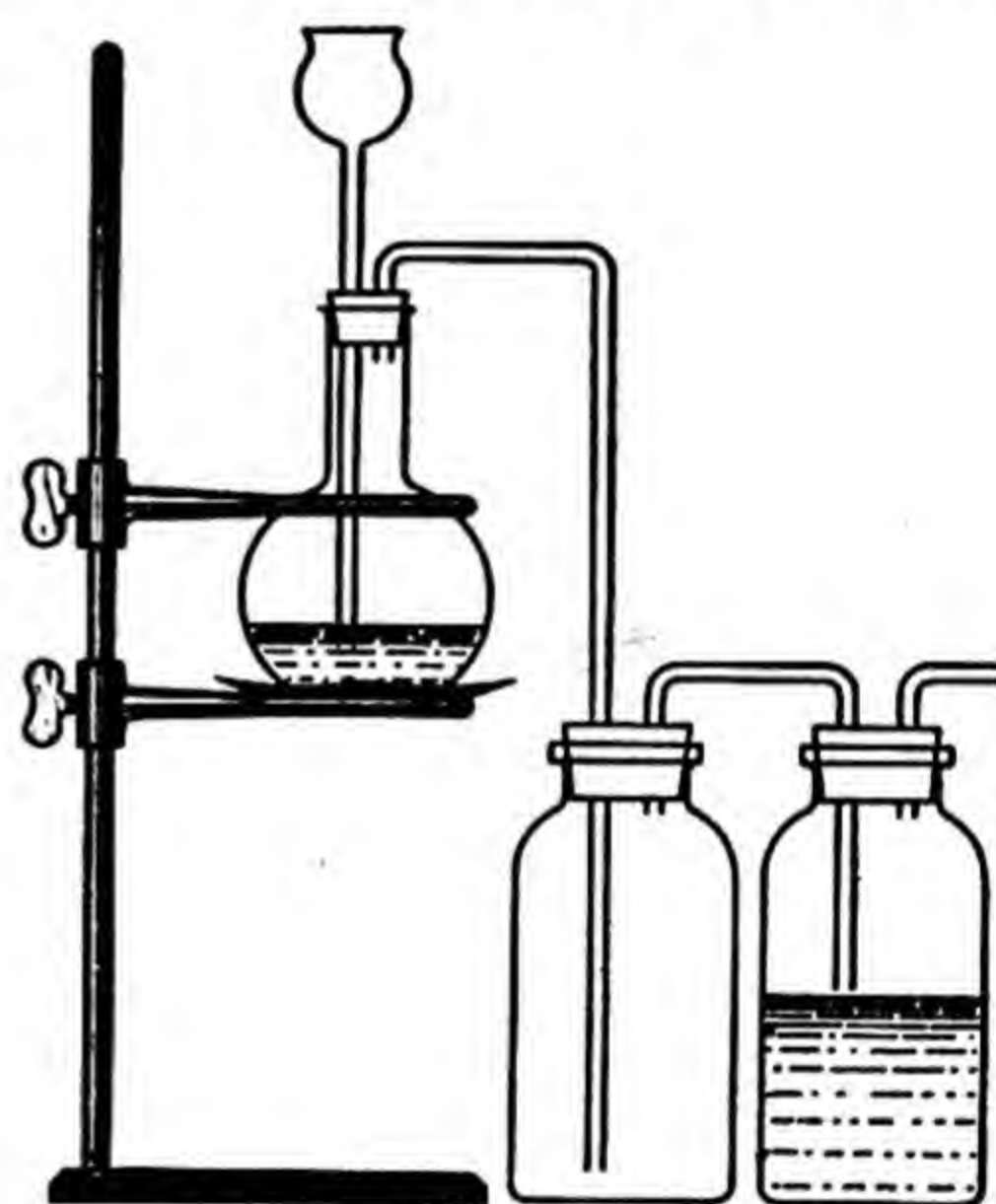


Fig. 116. A hydrogen chloride generator. Sulfuric acid acts upon sodium chloride, liberating hydrogen chloride gas.

because of the heat liberated when sulfuric acid is mixed with water.

The reaction between salt and sulfuric acid occurs in two steps. In the first step, one hydrogen atom of each sulfuric acid molecule takes the place of a sodium atom in a sodium chloride molecule:



In the second step, which requires a higher temperature and an excess of sodium chloride, the remaining hydrogen atom is replaced by sodium:



Physical properties. Pure hydrogen chloride is a colorless gas with a sharp, penetrating odor. It is extremely soluble in water, 1 liter of water dissolving about 450 liters of the gas at room

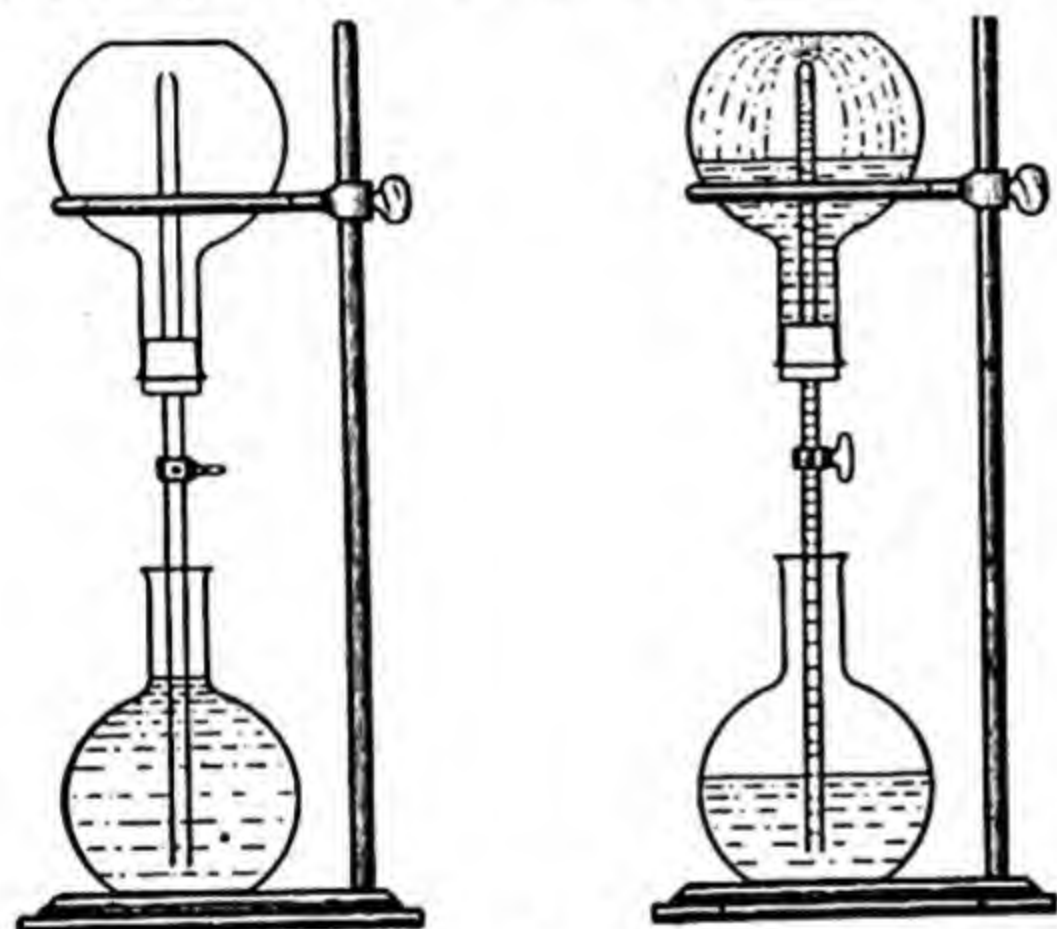


Fig. 117. The fountain experiment shows the extreme solubility of hydrogen chloride in water.

temperature and atmospheric pressure, forming hydrochloric acid. This solution is nearly 37 per cent hydrogen chloride by weight. A very dilute solution of hydrochloric acid has a sour taste.

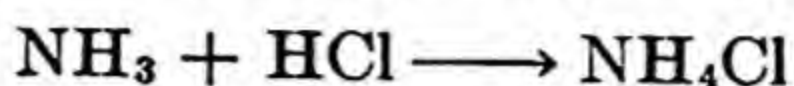
The extreme solubility of hydrogen chloride is illustrated by the fountain experiment shown in Fig. 117. The top bulb is filled with hydrogen chloride gas and the lower one with water. When the stopcock is opened, gas diffuses into the lower part of the tube joining the two flasks. There it dissolves in the water, causing a partial vacuum in the upper bulb. Owing to this partial vacuum, water rises in the tube, and as it does so it dissolves more gas. When water emerges from the jet in the upper flask, the dissolving action is so rapid that a fountain is produced.

Chemical properties. The chemical properties of hydrogen chloride differ from those of hydrochloric acid, which is hydrogen chloride dissolved in water. Hydrogen chloride is not easily decomposed. It is not very active. Only the most active of the metals, such as sodium, react with it:



When hydrogen chloride and ammonia gas (NH_3) meet, they form a dense white cloud composed of very small particles of a

white solid called ammonium chloride, NH_4Cl :



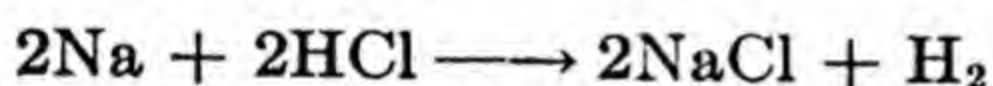
Hydrochloric acid is a typical acid. All acids have some properties in common:

1. They have a sour taste.
2. They change the color of litmus from blue to red.
3. They neutralize bases.
4. When placed on a metal like zinc or iron, they give up hydrogen, the metal taking the place of the hydrogen.

Hydrochloric acid reacts with bases or hydroxides to form water and a chloride. A typical reaction between hydrochloric acid and a base is represented by the equation



When hydrochloric acid comes in contact with metallic sodium, the metal replaces the hydrogen in the acid, forming sodium chloride and hydrogen:



This reaction is very violent, and it is not safe to perform the experiment in the laboratory.

With zinc the corresponding reaction is only moderately rapid, and this experiment may be performed with safety. Each zinc atom replaces two hydrogen atoms, forming zinc chloride:



Of the common metals, zinc, magnesium, iron, aluminum, and tin dissolve in hydrochloric acid. Mercury, silver, gold, and platinum are not soluble in this acid, and the action with tin is slow unless the mixture is heated. The reaction between a metal and hydrochloric acid is an example of *replacement*. In this reaction a metal atom replaces a hydrogen atom in an acid molecule.

Hydrochloric acid forms a curdy white precipitate of silver chloride when it is added to a solution of silver nitrate:



Silver chloride is insoluble in nitric acid. Silver nitrate is used to test a solution for any soluble chloride.

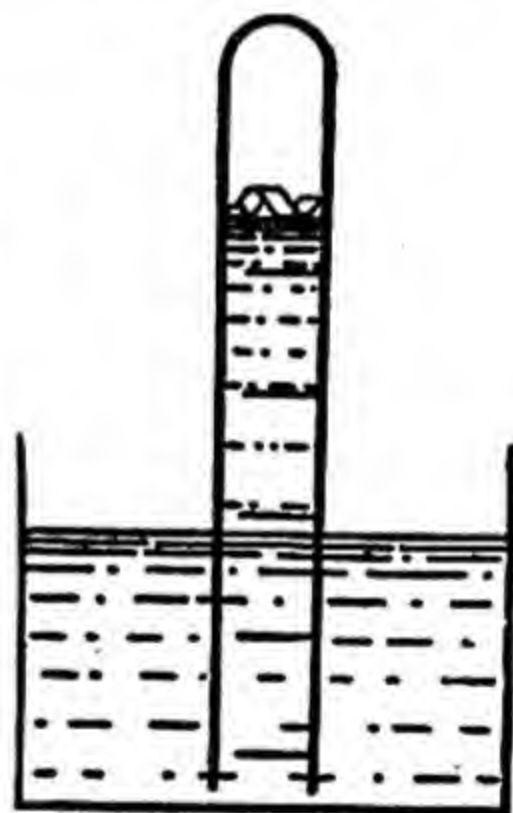
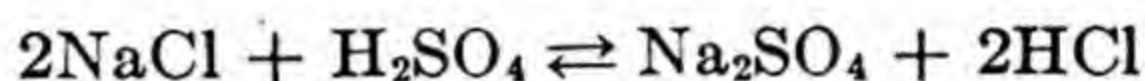


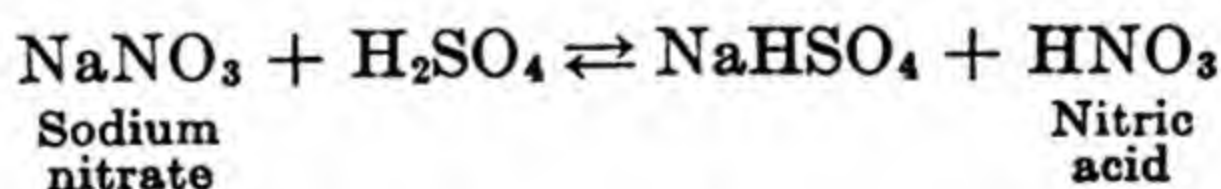
Fig. 118. Magnesium dissolves in dilute hydrochloric acid, liberating hydrogen gas.

Uses. Hydrochloric acid is used in the laboratory for making chlorine. Cornstarch, when heated with hydrochloric acid, forms glucose. Glue is extracted from bones through the use of hydrochloric acid. Metals are cleaned with hydrochloric acid before they are soldered or plated. Large quantities of hydrochloric acid are used in the preparation of ammonium chloride, which is used extensively in the manufacture of dry cells.

General method of preparing acids. The preparation of hydrochloric acid from sulfuric acid and salt is an application of a general method which can be used in the manufacture of many acids. A mixture of concentrated sulfuric acid and sodium chloride contains hydrogen chloride and sodium sulfate in addition to the original components. The mixture contains all of the substances shown in the following equation:



An arrow pointing each way indicates the possibility that the reaction may go in either direction. Of these four components, hydrogen chloride is the most volatile, and when the mixture is heated, the hydrogen chloride gas is driven out. *The most volatile component escapes.* If sulfuric acid were more volatile than any other substance represented in the equation, then sulfuric acid could be prepared by the action of hydrochloric acid on sodium sulfate (the reverse of the actual process). Nitric acid, being more volatile than sulfuric acid, is made by the action of sulfuric acid on a nitrate. Sodium hydrogen sulfate, NaHSO_4 , is a by-product of the reaction:



Questions and Exercises

1. Write an equation showing how hydrochloric acid is made from sodium chloride and sulfuric acid.
2. Name five metals which will react with hydrochloric acid, liberating hydrogen.
3. Write the equation for each of the reactions which are mentioned in Question 2.
4. Is it practical to collect hydrogen chloride gas over water? Explain.
5. In the preparation of hydrochloric acid, why should the exit tube from the generator be prevented from dipping below the surface of the water in the collecting bottle?
6. Distinguish between hydrogen chloride and hydrochloric acid.

7. Write a balanced equation for the reaction between hydrochloric acid and (a) zinc, (b) NaOH, (c) AgNO_3 .

8. Devise two methods for converting aluminum, Al, into aluminum chloride, AlCl_3 . Write an equation for each method.

9. How much sodium chloride would be required to produce 1000 g. of a 37 per cent solution of hydrochloric acid?

10. How many grams of sodium hydroxide will react with 3.65 g. of hydrochloric acid?

11. How many grams of hydrogen are produced when 36.5 g. of hydrochloric acid react completely with (a) sodium and (b) zinc?

12. State the physical and chemical properties of hydrogen chloride; of hydrochloric acid.

13. Describe a test for a dissolved chloride. What additional test would be required to identify the chloride as hydrochloric acid?

14. State four characteristics of acids.

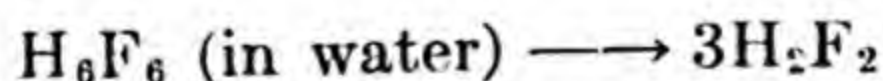
PART 4

Hydrofluoric Acid; Hydrobromic Acid; Hydriodic Acid

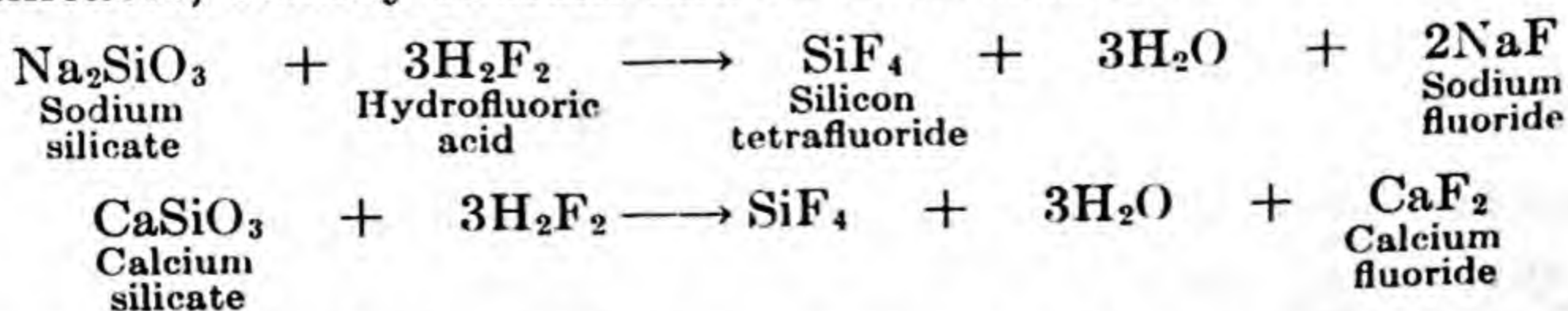
Hydrofluoric Acid

Preparation and properties. The compound hydrogen fluoride, formed by the union of hydrogen and fluorine, is a colorless gas. Its water solution is called *hydrofluoric acid*. In the gaseous state, unlike the other halogen acids, hydrogen fluoride tends to form associated molecules. Experimental evidence indicates that above 90°C., the formula for hydrogen fluoride is HF. At lower temperatures the formula seems to be H₂F₂. At still lower temperatures, H₆F₆ is formed. At 20°C. and under a pressure of 745 mm., 80 per cent of the hydrogen fluoride is associated in this way. When two or more molecules of a compound group themselves together to form a larger molecule, the substance is said to be *polymerized*, and the large molecule is said to be a *polymer* of the smaller one. The compound H₆F₆ is a polymer of HF.

Hydrogen fluoride is prepared by adding sulfuric acid to a fluoride. In all the important fluorides the element other than fluorine is a metal. When sulfuric acid acts upon a fluoride, the gas hydrogen fluoride leaves the solution. The escaping gas may be passed into water to form hydrofluoric acid:



This acid is of practical importance because of its use in etching glass; it attacks the silica in the glass. Glass is largely a mixture of silicates, usually sodium and calcium silicates.



The glass to be etched is covered with some nonreactive material such as paraffin, and lines or designs are cut through

this covering. Hydrofluoric acid is then placed on the exposed portion of the glass, with which it reacts. "Frosted" electric light bulbs and table glassware also are etched with hydrofluoric acid.

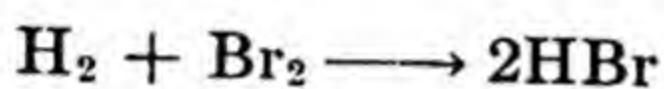
Since glass is a mixture of silicates, a glass bottle cannot be used as a container for hydrofluoric acid. Bottles made of hard paraffin are used. Since the acid also reacts with the skin and with the fingernails, great care must be exercised in handling it.

Hydrofluoric acid is used also to remove the sand from iron castings, in cleaning the exteriors of stone buildings, and in dissolving complex silicates.

Sodium fluoride, a salt of hydrogen fluoride, is used in ant powder and other insecticides.

Hydrobromic Acid

Preparation. Hydrogen bromide, like the corresponding chlorine compound, may be prepared by burning hydrogen in the halogen vapor:

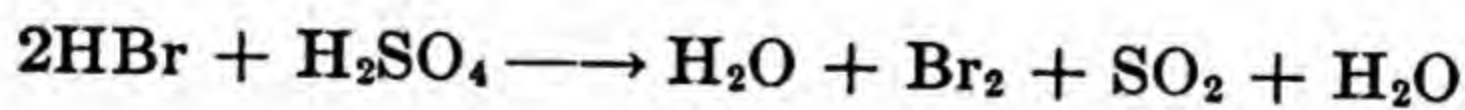


This reaction is very slow and is seldom used.

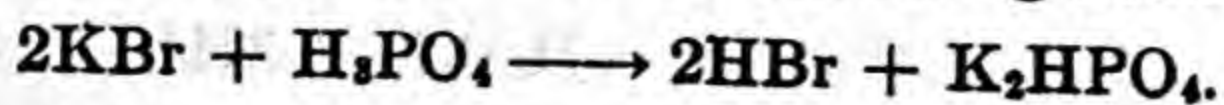
Pure hydrogen bromide cannot be formed by the action of concentrated sulfuric acid on sodium or potassium bromide, a method corresponding to the preparation of hydrogen chloride. The reaction



takes place at first, and colorless hydrogen bromide, which fumes in moist air, can be detected. However, the contents of the flask soon turn dark brown, the color of free bromine. At the same time the odor of burning sulfur is noticed. This is sulfur dioxide, SO_2 . A secondary reaction takes place in which one atom of oxygen is given up by each molecule of the sulfuric acid which takes part in the reaction. This changes the sulfuric acid, H_2SO_4 , to sulfurous acid, H_2SO_3 . Sulfurous acid breaks down into SO_2 and water. The oxygen released by the acid oxidizes the hydrogen atoms in two molecules of hydrogen bromide, forming water and leaving free bromine:

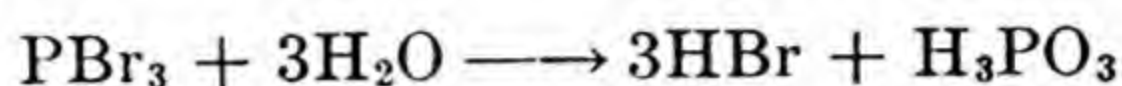


Pure hydrobromic acid may be formed, however, by using phosphoric acid, H_3PO_4 , in place of sulfuric acid. Phosphoric acid has a high boiling point and no oxidizing action.



Only two of the three hydrogen atoms in phosphoric acid are easily replaced.

Hydrogen bromide is often formed in the laboratory by allowing water to fall, a drop at a time, on a mixture of red phosphorus and bromine. Phosphorus tribromide is formed when phosphorus and bromine are mixed:

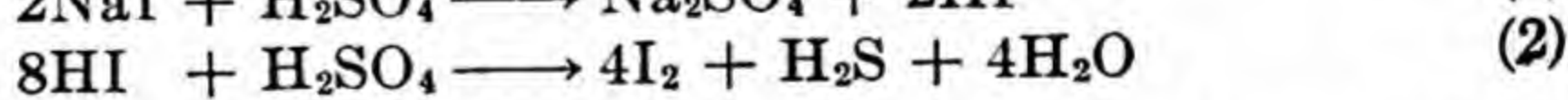
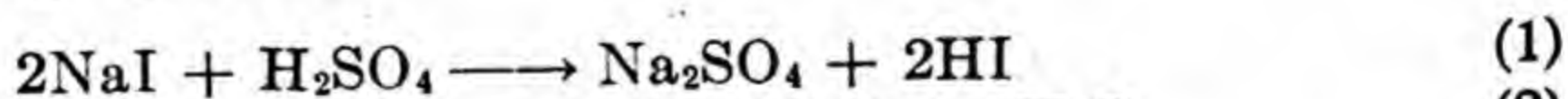


Properties of hydrogen bromide and of hydrobromic acid. Hydrogen bromide, like hydrogen chloride, is a gas which is very soluble in water. Hydrobromic acid is a typical acid, with properties similar to those of hydrochloric acid.

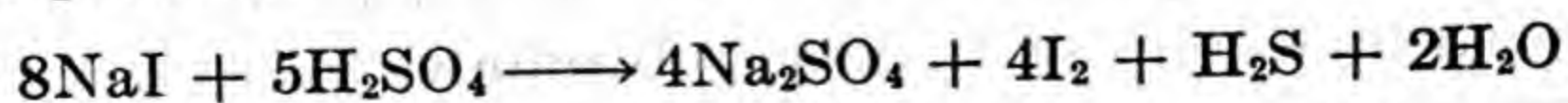
Bromides find a limited use in medicine as sedatives. They are used on a large scale in the manufacture of photographic emulsions, which usually consist of silver bromide particles suspended in gelatin.

Hydriodic Acid

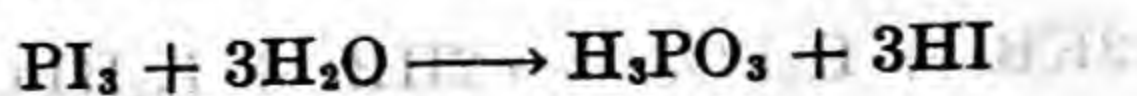
Preparation and properties. Hydrogen iodide, a colorless gas, dissolves readily in water, forming hydriodic acid. In chemical properties it resembles hydrochloric and hydrobromic acids. It is impossible to prepare hydrogen iodide by the action of concentrated sulfuric acid on an iodide. It is much less stable than hydrogen bromide, and takes all of the oxygen from the sulfuric acid molecule, reducing the latter to H_2S . This oxygen removes the hydrogen from molecules of HI , oxidizing them to water and leaving free iodine. The reactions may be represented by the following equations:



Since the hydrogen iodide, HI , formed in reaction (1) is oxidized immediately, we may write the following single equation for the complete process:



The practical method for making hydriodic acid is to allow water to fall, a drop at a time, on a mixture of iodine and red phosphorus. Iodine and phosphorus form phosphorus iodide, PI_3 , and this is decomposed by water with the production of hydrogen iodide and phosphorous acid:



The hydrogen iodide, being a gas, escapes from the mixture and can be collected in water.

Test for a Bromide or Iodide

We have learned that the test for a chloride consists in adding a solution of silver nitrate to a solution of the salt to be tested. A white, curdy precipitate, insoluble in nitric acid, is formed if the solution contains a chloride. Unfortunately, bromides and iodides also form precipitates with silver nitrate (AgBr and AgI). These precipitates are pale yellow in color, but may be confused with silver chloride. If we are uncertain as to whether the solution we are testing is a chloride, a bromide, or an iodide, we can easily distinguish between the three in the following way: Place the solution in a test tube. Add about 2 cc. of carbon tetrachloride or chloroform. Next add a few drops of a solution of chlorine in water, and shake the contents of the test tube vigorously. If the substance is a chloride, no reaction takes place; if it is a bromide or an iodide, the element (bromine or iodine) will be freed by the chlorine, and will dissolve in the carbon tetrachloride. If bromine is present, the carbon tetrachloride will be colored a brownish red. The color will be violet if iodine is present.

Questions and Exercises

1. Write an equation for the reaction between hydrofluoric acid and calcium silicate, CaSiO_3 .
2. How is hydrofluoric acid made?
3. Why is hydrofluoric acid kept in paraffin bottles?
4. Why is it not practical to make hydrobromic acid from sodium bromide and sulfuric acid?
5. How could you distinguish sodium chloride from sodium bromide?
6. Free iodine imparts a blue color to starch paste, but neither chlorides nor iodides color starch paste. How could you use the starch test to determine whether an unknown salt is a chloride or an iodide?
7. How would you distinguish between hydrogen bromide and bromine?
8. Write equations for the preparation of hydrobromic acid and hydriodic acid. Which of these acids is the better reducing agent? Give a reason for your answer.
9. How many grams of hydrogen fluoride gas are formed by the action of sufficient sulfuric acid on 312 g. of calcium fluoride?
10. Write the equation for the reaction of each of the four halogen acids with sodium hydroxide.
11. How could you identify hydrogen fluoride? Could you set its fluorine free by means of some other halogen?

12. How could you distinguish between potassium bromide and potassium iodide?

13. Prepare a table of the halogens in the following form:

(a) Elements in order of atomic weights	(b) Atomic numbers	(c) Color	(d) Boiling point	(e) Physical state (gas, liquid, or solid)
(f) Equations for the preparation of the element	(g) Equations for the preparation of the hydrogen compound	(h) Elements in order of replacing power	(i) Elements in order of chemical activity	

PART 5

Oxygen Compounds of the Halogens

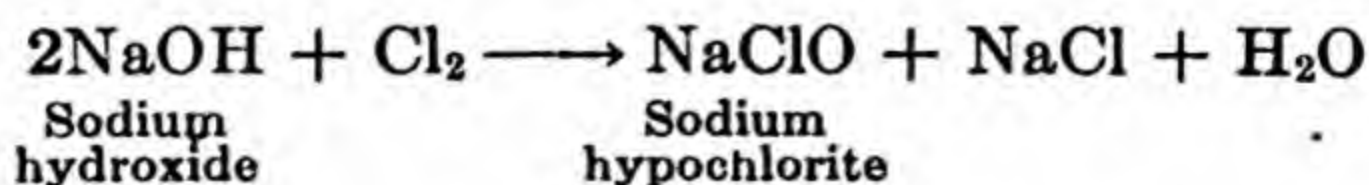
Oxygen compounds of the halogens. Fluorine forms a fairly stable compound with oxygen, having the formula F_2O . At low temperatures, F_2O_2 and F_2O_3 can be made. Bromine forms no stable oxides, but two unstable oxides having the formulas Br_2O and BrO_2 , have been prepared. Chlorine forms the oxides Cl_2O , ClO_2 , and Cl_2O_7 ; and iodine, the two oxides I_2O_4 and I_2O_5 . These oxides are not formed by direct union of the elements.

Oxygen acids of the halogens. Several acids are known in which chlorine, bromine, and iodine are combined with both hydrogen and oxygen. They are unstable compounds, and they decompose readily. Some of them have never been obtained in the pure state but only in solution. Salts of these acids are stable enough to be easily prepared, but they all decompose when heated and they are all good oxidizing agents.

OXYGEN ACIDS OF CHLORINE

Valence of Cl	Formula of Acid	Name of Acid
-1	$HClO$	Hypochlorous
-3	$HClO_2$	Chlorous
-5	$HClO_3$	Chloric
-7	$HClO_4$	Perchloric

Pure hypochlorous acid, $HClO$, has not been obtained in the free state. Salts of this acid are called hypochlorites. They are made by dissolving chlorine in cold, dilute solutions of bases:



The familiar odor of bleaching powder is due to hypochlorous acid, liberated by the carbonic acid of the air.

molecule has been replaced by a metal, forming a salt, the ending *ide* is given to the nonmetallic element.

HCl = hydrochloric acid

HBr = hydrobromic acid

HI = hydriodic acid

H₂S = hydrosulfuric acid

NaCl = sodium chloride

KBr = potassium bromide

MgI₂ = magnesium iodide

FeS = iron sulfide

The names of acids which contain oxygen in their molecules in addition to the two other elements end in either *ous* or *ic*. If there are two oxygen acids of the same element, the one which contains the greater number of oxygen atoms is given the *ic* ending; that which contains less oxygen is given the ending *ous*. For example, HClO₃ is called *chloric acid*, while HClO₂, which contains one less atom of oxygen in its molecule, is called *chlorous acid*. When a metal has displaced the hydrogen of the acid, forming a salt, the salt derived from the *ic* acid is given the ending *ate*. In like manner *ous* acids give *ite* salts. For example, chloric acid has the formula HClO₃, and its salts, KClO₃, NaClO₃, are called potassium *chlorate* and sodium *chlorate*, respectively. The corresponding salts of chlorous acid, KClO₂ and NaClO₂, are called potassium *chlorite* and sodium *chlorite*.

If there are more than two oxygen acids composed of the same elements, the acid with more oxygen in the molecule than the *ic* acid is given the prefix *per*. Perchloric acid, HClO₄, is an example. It contains one more oxygen atom than chloric acid, HClO₃. If an acid exists with one less oxygen atom than the *ous* acid, it is given the prefix *hypo*. Hypochlorous acid, HClO, illustrates this

NOMENCLATURE OF ACIDS AND SALTS

Acid			Salt		
Scheme	Example		Scheme	Example	
	Name	Formula		Name	Formula
per—ic	perchloric acid	HClO ₄	per—ate	potassium perchlorate	KClO ₄
—ic	chloric acid	HClO ₃	—ate	potassium chlorate	KClO ₃
—ous	chlorous acid	HClO ₂	—ite	potassium chlorite	KClO ₂
hypo—ous	hypochlorous acid	HClO	hypo—ite	potassium hypochlorite	KClO
hydro—ic	hydrochloric acid	HCl	—ide	potassium chloride	KCl

use. The accompanying table of the chlorine oxygen acids and their salts shows the custom followed in naming oxygen acids and their corresponding salts.

Questions and Exercises

1. Write the formulas for the acids from which the following salts are derived: Na_2SO_4 , NaBr , NaNO_3 , Na_3PO_4 , and NaClO_3 .
2. Write the formulas and names (a) of the oxygen acids of bromine; (b) of the sodium salts corresponding to each of them.
3. Iodic acid has the formula HIO_3 . Name the following salts: (a) KIO_3 , (b) KIO_2 , (c) KIO_4 , (d) KIO .
4. If sulfuric acid has the formula H_2SO_4 , write the formula for (a) sulfurous acid, (b) persulfuric acid, (c) hyposulfurous acid.
5. Name the potassium salts of the sulfur acids mentioned in Question 4.
6. What property of the chlorates makes them useful for fireworks? Write an equation showing the decomposition of sodium chlorate. (See page 41.)
7. What weight of oxygen can be obtained by the decomposition of 426 g. of sodium chlorate?

UNIT VII

Acids, Bases, and Salts; Ionization; Colloids

PART 1

Acids, Bases, and Salts

A large number of the compounds that are used in the laboratory are either acids, bases, or salts. We have already studied the properties of several acids, namely those formed by the halogens; and we have learned that the metals in Group I of the Periodic Table form bases. We have learned also that acids neutralize bases, forming salts. We shall now study these three classes of substances in more detail.

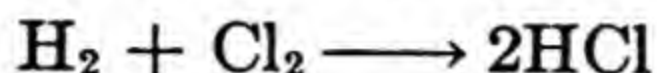
Acids

When we hear the name "acid," we are likely to think of a liquid which, when spilled upon the skin, causes a burn. Acids like sulfuric acid and nitric acid, especially in the concentrated form, do act in this way, but many others do not. A sour taste is a property of all acids. The taste of vinegar is due to acetic acid. Citric acid occurs in oranges, lemons, and grapefruit. Oxalic acid is present in rhubarb, malic acid in green apples, and lactic acid in sour milk. Carbonic acid is present in ordinary soda water. These acids do not have the destructive action of sulfuric acid or nitric acid. Neither do they taste as sour as sulfuric, nitric, hydrochloric, and phosphoric acids. The last four acids are called *strong* acids; the others are *weak* acids.

Each of the acids mentioned above contains at least one hydrogen atom in combination with some other element or a group of elements (radical). Nearly all acids contain hydrogen atoms which can be replaced by metals. We must remember, however, that not every compound which contains hydrogen is an acid. Sugar, glucose, and starch are not acids, although they have hydrogen atoms in their molecules. The hydrogen must be combined with an acid radical. This may be a nonmetal like chlorine, as in HCl , or a group of atoms like the sulfate radical (SO_4) in H_2SO_4 , the nitrate radical (NO_3) in HNO_3 , and the phosphate radical (PO_4) in H_3PO_4 .

We shall use in the laboratory, in this course, mainly the four strong acids: hydrochloric, sulfuric, nitric, and phosphoric. We shall therefore confine our study of acids to these four.

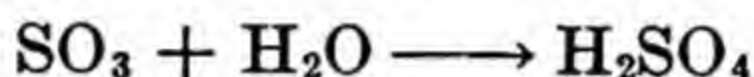
Preparation of acids. Hydrochloric acid may be prepared by the direct combination of its element:



It is usually prepared by the general method for making acids, wherein concentrated sulfuric acid is allowed to act on a salt of the desired acid:



Sulfuric acid is formed by dissolving its *acid anhydride*, SO_3 , in water:

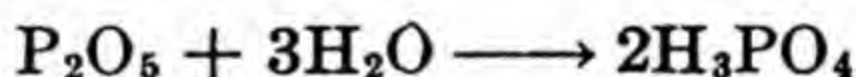


An acid anhydride is an oxide which, when dissolved in water, forms an acid.

Nitric acid is produced by the reaction between concentrated sulfuric acid and a nitrate, usually sodium nitrate:



Phosphoric acid may be prepared by dissolving its acid anhydride, P_2O_5 , in water:

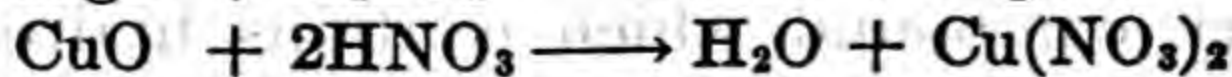


Reactions of acids. We have said that acids contain hydrogen which is replaceable by metals. This property was made use of in the preparation of hydrogen:

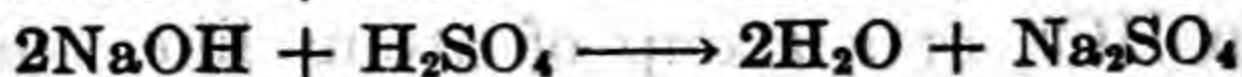
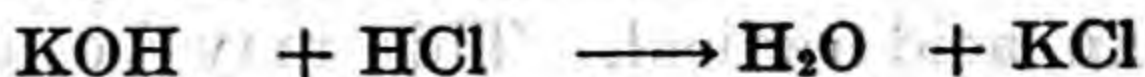


An acid will react also with the oxide of a metal or the hydroxide of a metal to form water and a salt:

Reactions with oxides:



Reactions with hydroxides:



Bases

We have studied the properties and methods of preparing the hydroxides of the alkali metals. Sodium hydroxide and potassium hydroxide are the most important of these compounds. They are called *bases*. Among the many other bases which we shall use frequently in the laboratory are calcium hydroxide, a solution of which is called limewater; barium hydroxide, $\text{Ba}(\text{OH})_2$; magnesium hydroxide, $\text{Mg}(\text{OH})_2$; ferric hydroxide, $\text{Fe}(\text{OH})_3$; aluminum hydroxide, $\text{Al}(\text{OH})_3$; and ammonium hydroxide, NH_4OH .

Each of these bases consists of a metal (or the NH_4 group, which acts like a metal) combined with one or more OH groups (hydroxide radicals). The metal in each case has lost an electron to each OH radical. A broader definition of a base will be considered later.

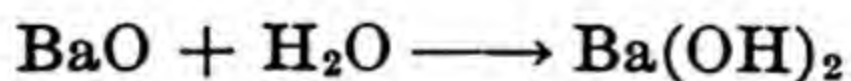
Preparation of bases. A review of the preparation of sodium and potassium hydroxides reminds us of some of the general methods for making bases.

Calcium hydroxide is made by dissolving the *basic anhydride*, quicklime, or unslaked lime, CaO , in water. You may have seen masons mixing quicklime with sand and water when making mortar. Whitewash is made by treating quicklime with water alone. In each of these operations the lime reacts with water, forming calcium hydroxide, $\text{Ca}(\text{OH})_2$, some of which dissolves in the excess of water. The mixture becomes very hot during the process, as it is an exothermic reaction. The temperature of the water may be raised to the boiling point. The reaction that takes place is represented by the equation:

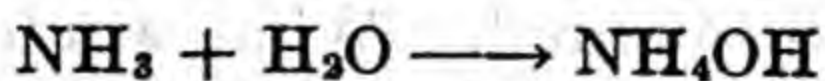


Calcium is in Group II of the Periodic Table, and has a valence of 2. It gives up two valence electrons to an oxygen atom when it forms the oxide CaO . When this reacts with water, each calcium atom holds two hydroxide radicals.

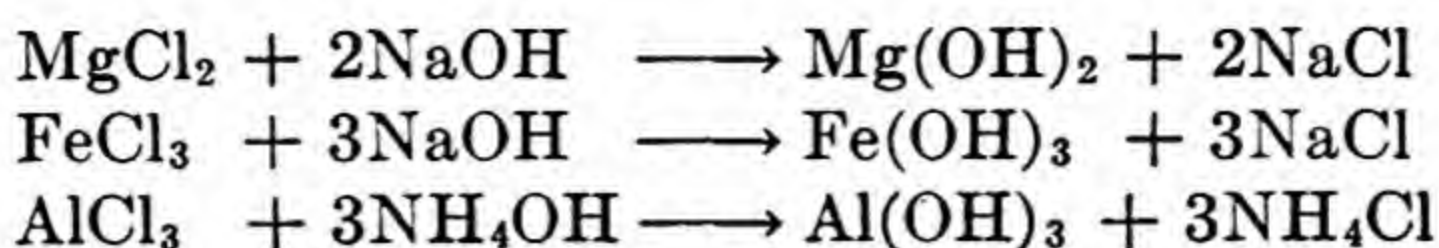
Barium hydroxide also is formed by dissolving the anhydride in water:



Ammonium hydroxide is made by dissolving ammonia gas, NH_3 , in water:



Magnesium hydroxide, ferric hydroxide, and aluminum hydroxide are very slightly soluble in water, and are prepared by adding the solution of a soluble base to a solution of a salt of the metal:



The hydroxide separates from the solution as a precipitate. This precipitate is filtered and washed with water to free it from any excess of chemicals used. When the hydroxide, Ca(OH)_2 , is heated, water is driven off and calcium oxide, CaO , is obtained. The residue left when water is driven from a hydroxide is called a basic anhydride. Ferric hydroxide, Fe(OH)_3 , when heated, loses water, leaving a residue of Fe_2O_3 , the basic anhydride of ferric hydroxide.

Salts

Neutralization: formation of water and a salt. We have said that bases and acids neutralize each other. What do we

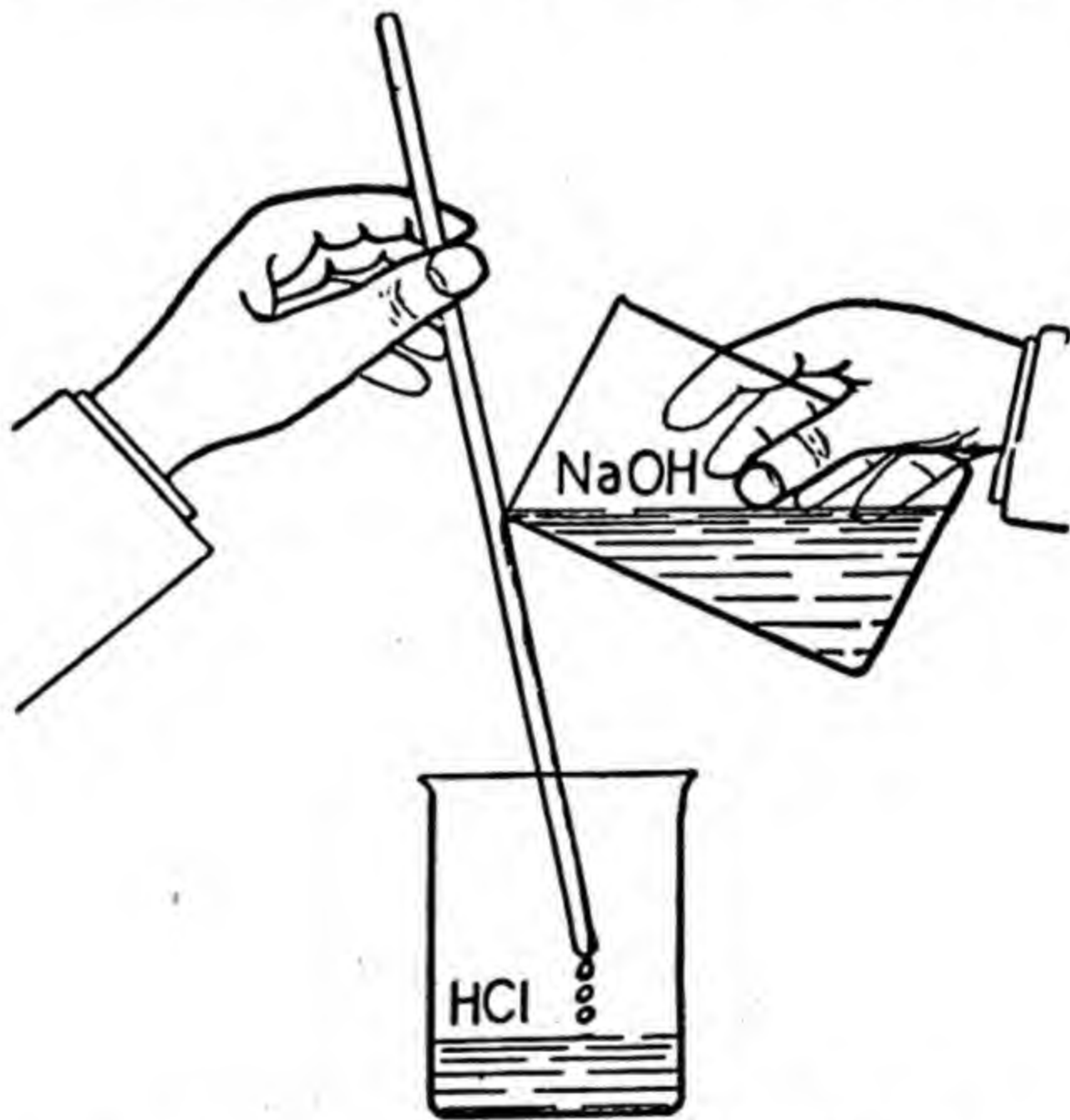


Fig. 119. A colored indicator such as litmus, phenolphthalein, or methyl orange is used to show the neutral point when an acid is neutralized by a base.

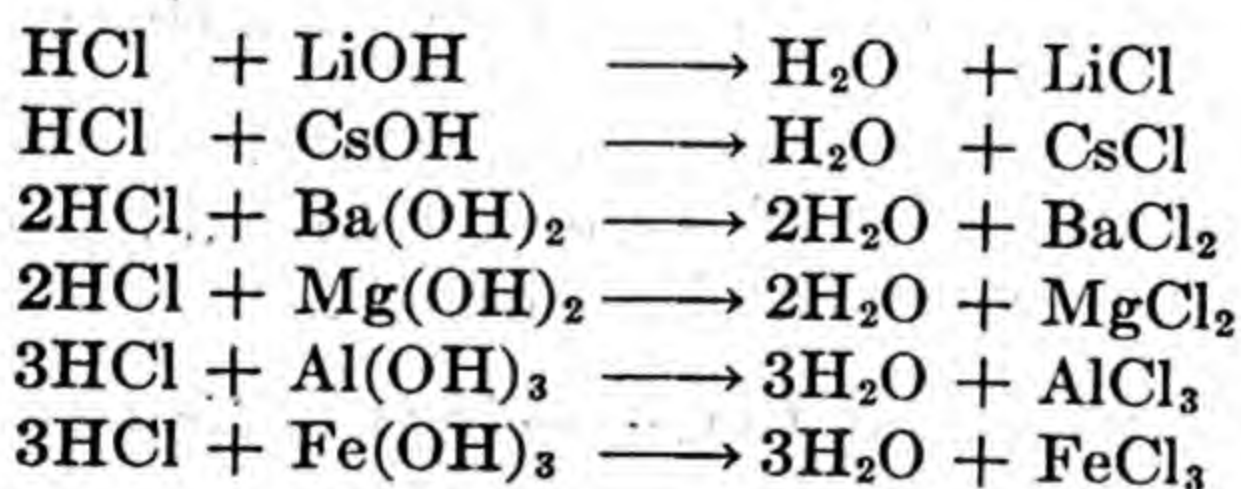
mean by such a statement? The effect of bases on litmus is exactly the reverse of that of acids. Bases turn red litmus blue, while acids turn blue litmus red. What would happen if we were to add the same number of hydrochloric acid molecules and sodium hydroxide molecules to a solution of neutral litmus? We should find that the litmus was neither blue nor red, but a color between the two—lavender. At the same time the solution con-

taining equal numbers of HCl and NaOH molecules no longer tastes sour like an acid, or brackish like a base. It has a salty taste—the taste of sodium chloride. When an acid and a base react, the resulting solution has the properties of neither of the original substances, and therefore we say that the acid and base have neutralized each other. The hydrogen of the acid and the hydroxide radical of the base have combined to form water, which has a neutral reaction on litmus; that is, the water does not change the color of an indicator. Water also has no taste. The solution resulting from the neutralization of an acid and a base has the taste of a salt. If we were to neutralize potassium hydroxide with sulfuric acid, the salt remaining in solution would be potassium sulfate:



A salt is the substance, in addition to water, which is formed when an acid and a base neutralize each other.

We may define a salt by saying that it is *a compound derived from an acid by replacing the hydrogen atoms of the acid by a metal or by the ammonium radical*. This replacement may be accomplished by neutralizing the acid with a base. We might expect that each acid would form as many salts as there are metals, since metals are base formers. This expectation is true, in general. The following equations represent the formation of a number of chlorides—salts formed by the neutralization of hydrochloric acid with various bases:



Acid salts. When an acid and a base neutralize each other, exactly the same number of hydrogen atoms from the acid and hydroxide radicals from the base unite to form water:



If we wish to neutralize sulfuric acid, H_2SO_4 , we should have to add twice as many molecules of sodium hydroxide as we have molecules of sulfuric acid, because each molecule of sulfuric acid contains two replaceable hydrogen atoms. It requires two molecules of sodium hydroxide, each containing one OH group, to

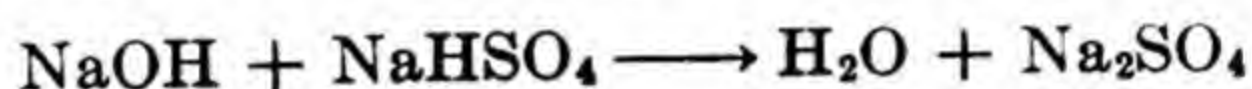
neutralize these two hydrogen atoms. Two molecules of water are formed in the reaction:



What would happen if we were to add sodium hydroxide to sulfuric acid, molecule for molecule? Would the sodium hydroxide completely neutralize half of the sulfuric acid molecules present, leaving a solution of sodium sulfate and some unneutralized sulfuric acid? We find by experiment that one of the hydrogen atoms of each molecule of sulfuric acid is removed by the base, according to the reaction:



The salt formed is sodium hydrogen sulfate, sometimes called *acid sodium sulfate* or *sodium bisulfate*. This is an *acid salt*—a salt which still possesses some properties of an acid. The salt will react with a second molecule of sodium hydroxide, during which process the second hydrogen atom becomes neutralized:



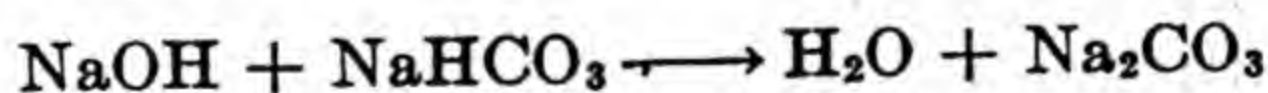
Sodium sulfate is called a *normal salt*. It contains no replaceable hydrogen and has no acid properties.

Carbonic acid is an acid which also may be neutralized in two steps. With equimolecular mixtures of acid and base, the bicarbonate is formed:



Bicarbonate of soda is ordinary baking soda.

With another molecule of sodium hydroxide, normal sodium carbonate is formed from the bicarbonate:



The reaction may be carried to the final stage in one step by using two molecules of sodium hydroxide for each molecule of carbonic acid present:



Questions and Exercises

1. Write equations for the formation of several salts of sulfuric acid by the neutralization of this acid with bases.

2. Write equations for the formation of two acid salts and the normal salt of phosphoric acid when neutralized with potassium hydroxide.

3. Write the formula of a substance in each of the following classes: acid; base; basic anhydride; normal salt; acid anhydride; acid salt; chloride; perchlorate sulfate.

4. Classify each of the following as an acid, base, salt, acid anhydride, or basic anhydride: P_2O_5 ; HNO_3 ; $Be(OH)_2$; $CaSO_4$; $KClO_3$; MgO ; $CsOH$; SO_3 ; $Fe(OH)_2$; Na_2CO_3 ; SO_2 . Write the name of each compound.

5. Give the name of the acid and of the base which would be used to form each of the following salts by neutralization: lead chloride, $PbCl_2$; potassium chlorate, $KClO_3$; copper sulfate, $CuSO_4$; barium chloride, $BaCl_2$; ferric phosphate, $FePO_4$; calcium carbonate, $CaCO_3$; lithium nitrate, $LiNO_3$; sodium chlorite, $NaClO_2$; ammonium phosphate, $(NH_4)_3PO_4$.

6. Name the element which is common to all acids.

7. State three properties common to all acids.

8. Name three properties common to all bases.

9. In which groups of the Periodic Table do the base-forming elements occur?

10. Where do the acid-forming elements occur in the Periodic Table?

11. Write the formula for a common acid and for an important base. Write an equation for the reaction which takes place when these two compounds are mixed.

12. Calculate the weight of hydrochloric acid necessary to neutralize 80 g. of sodium hydroxide.

13. How many grams of potassium sulfate are formed when 392 g. of sulfuric acid are completely neutralized by potassium hydroxide?

14. State the effect of each of the following on both red and blue litmus paper: (a) a solution of sulfuric acid; (b) a solution of calcium hydroxide; (c) a solution containing an equal number of molecules of sulfuric acid and calcium hydroxide.

15. How would you prepare normal sodium carbonate from sodium bicarbonate?

16. How many grams of potassium sulfate, K_2SO_4 , are formed by the action of an excess of potassium hydroxide on 272 g. of acid potassium sulfate?

PART 2

Ionization: Conductors and Nonconductors of Electricity

Acids, bases, and salts possess several properties in common—one of these is the capacity to conduct electricity when dissolved in water or when in the molten state. When we speak of a conductor of electricity, we usually think of a metal. All metals conduct electricity; most nonmetals do not. Sulfur, glass, porcelain, rubber, and many other nonmetallic substances are used as *insulators* in electrical work. We see some of these in use when we observe a telegraph pole on which wires bearing electric currents are fastened to glass or porcelain insulators.

Pure water is a poor conductor of the electric current. We can easily perform an experiment to show that water solutions of acids, bases, and salts conduct a current, while solutions of other substances do not.

Anyone who has done electrical wiring knows that there must be no breaks in the wire through which the current is flowing. If there is a break, an ordinary current of low voltage will not pass, since dry air is a nonconductor of electricity. If air were as good a conductor as is copper, our doorbells would ring continuously and our electric lights would burn day and night. We can, however, ring our bells and light our electric bulbs at will by merely leaving a break in the wire which is bridged by a piece of metal when we press a button or throw an electric switch. If a current of electricity is to keep flowing, every part of the circuit must consist of a conductor.

Let us connect an electric light bulb, by means of a pair of copper wires, to a source of an electric current. Electrons flow through the wire and through the filament in the bulb, heating the filament to a white heat so that it gives out light. Now let us cut one of the wires leading to the filament and fasten securely to each of its ends a small strip or rod of copper.

If these metallic strips, called electrodes, are now immersed in distilled water without being in contact with each other, the bulb will not glow. The electrodes are separated by distilled water, and since pure water is practically a nonconductor of elec-

tricity and will not allow electrons to pass through it, the light does not glow. Glass or rubber clamps are used in the apparatus shown in Fig. 120, for iron is a good conductor of electricity. The circuit would be closed through the ring stand if metal clamps were used. If some crystals of sugar are dissolved in the water, there is still no evidence of light in the bulb, showing that a solution of sugar is a nonconductor of electricity. If, however, we add a few drops of hydrochloric acid to distilled water in the beaker, the lamp glows brightly. A solution of hydrochloric acid, therefore, permits electrons to pass through the lamp filament almost as readily as they did before the wire was broken.

We may now use this simple apparatus to determine which substances are *electrolytes*, and which are *nonelectrolytes*. An *electrolyte* is a substance which, when dissolved in water, conducts an electric current. The solution of a *nonelectrolyte* does not conduct an electric current. We merely place a solution of the substance to be tested in the beaker, with the connections indicated in Fig. 120, and observe the lamp. The results of such experiments are indicated below.

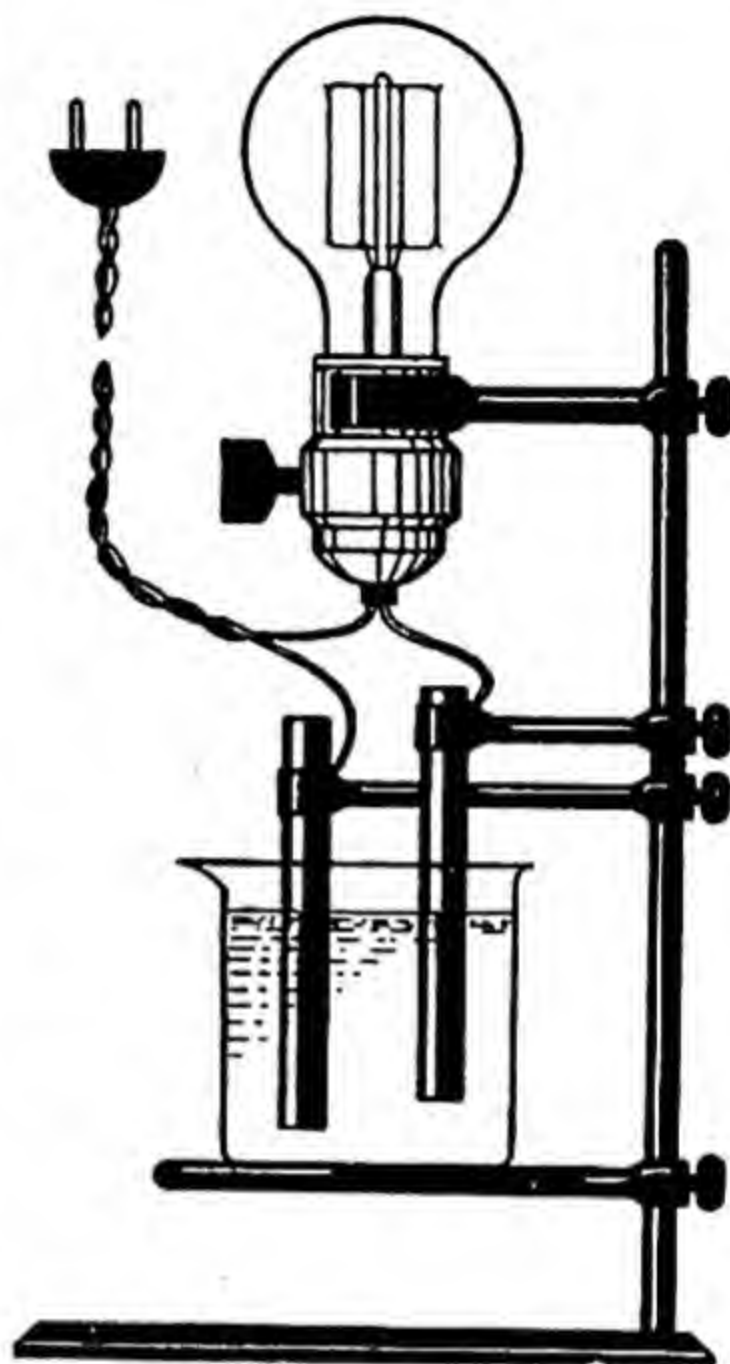


Fig. 120. A light circuit with a connection through distilled water or through a solution.

BEHAVIOR OF THE LAMP WITH VARIOUS SUBSTANCES DISSOLVED IN WATER

<i>Bright Light</i>	<i>No Light</i>	<i>Dim Light</i>
Hydrochloric acid	Distilled water	Acetic acid
Sulfuric acid	Alcohol	Ammonium hydroxide
Nitric acid	Sugar	Butyric acid
Sodium hydroxide	Glycerin	Oxalic acid
Potassium hydroxide	Starch	Citric acid
Calcium hydroxide	Glucose	Lactic acid
Sodium chloride	Acetone	
Phosphoric acid	Benzene	
Potassium sulfate	Camphor	
Sodium nitrate		
Sodium carbonate		
Copper chloride		

Other properties of electrolytes. (1) We have learned that the vapor pressure of a solvent is lowered when a solute is dissolved in the liquid, and that this lowering is proportional to the number of solute molecules present in a given weight of solvent. If, for example, we were to dissolve one mole of sugar (342 grams or

6×10^{23} molecules) in 1000 g. of water, we should find the vapor pressure of the solution to be equal to approximately 98 per cent of the vapor pressure of pure water at the same temperature. The vapor pressure of water is lowered about 2 per cent by the addition of one mole of sugar to 1 liter of water. If we dissolve a mole of a salt, like sodium chloride, in 1000 g. of water, we find that the lowering of the vapor pressure is almost double the lowering which was obtained in the case of the sugar solution. Since a mole of any substance contains the same number of molecules, the molecular concentration of the solute in the two solutions should be the same.

(2) When a mole of sugar is dissolved in 1000 g. of water, the solution boils at $100.518^{\circ}\text{C}.$, or 0.518° above the boiling point of pure water. The same solution freezes at $1.86^{\circ}\text{C}.$ below the freezing point of pure water, $0^{\circ}\text{C}.$ One mole of sodium chloride in 1000 g. of water produces an elevation of the boiling point of water nearly twice as great as that caused by the mole of sugar. The same salt solution depresses the freezing point almost twice as much as the sugar solution does.

When a solution containing one mole of barium chloride, BaCl_2 , is dissolved in 1000 g. of water, the depressions of the vapor pressure and of the freezing point, and the elevation of the boiling point, are almost three times as great as the corresponding effects caused by a molal solution of sugar or any other nonelectrolyte. All strong electrolytes—the compounds which give a bright light when an electric current is passed through their solutions—act in a manner analogous to the action of common salt. Solutions of weak electrolytes, which show only a dim light, give only a slightly abnormal depression of the vapor pressure, of the freezing point, and only a slight increase in boiling point.

The results of these experiments indicate that electrolytes in aqueous solution do not exist entirely in the molecular form, but are broken down into smaller units. Each of these units has the same effect on the vapor pressure of a solution as does an entire molecule.

The theory of ionization. Arrhenius, a Swedish chemist, was the first to explain the conduction of an electric current by solutions. He proposed the theory that substances which conduct the current exist, in water solution, in the form of ions. An ion is an atom or radical (a group of atoms) possessing an electric charge. Some ions are positive and others are negative. We learned that when sodium and chlorine unite to form sodium chloride, each sodium atom loses an electron and each chlorine atom gains an electron.

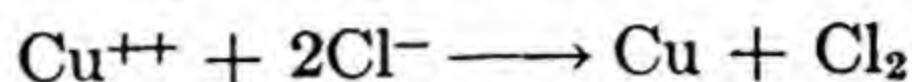
After this transfer of electrons has occurred, the atoms are electrically charged. The sodium atom, having lost one negative charge, is a positively charged sodium *ion*. A negatively charged chlorine atom is called a *chloride ion*. Many of these ions are held together in the crystalline form, as shown in Fig. 19 (page 24), owing to the electrical attraction between ions of opposite charge. We use a plus (+) sign to show the presence of a positive charge and a minus (−) sign to indicate a negative charge. The symbol for the sodium ion is Na^+ , and that for the chloride ion is Cl^- . When sodium chloride is dissolved in water, the ions separate, and in very dilute solutions they are practically independent of each other. In a similar manner, copper chloride is formed by the transfer of the two valence electrons of copper to two chlorine atoms, forming a salt with the formula CuCl_2 . When copper chloride is dissolved in water, as in the case of sodium chloride, the ions separate, forming a copper ion with a charge of plus 2, its symbol being Cu^{++} . Two chloride ions are formed at the same time.

Electrolysis. Let us see what happens to these copper ions and chloride ions when electrodes made of platinum are immersed in the solution and connected with dry cells and the light bulb. The brilliant light tells us that electrons are passing rapidly through the filament. What is taking place in the solution of copper chloride at the same time?

One terminal of the battery has an excess of electrons and is electrically negative. It is called the *cathode*. The other terminal of the battery is positively charged. The positive electrode is called the *anode*. Since opposite electrical charges are attracted to each other, the positive copper ions (cations) pass through the solution to the cathode. At the same time, the negative chloride ions (anions) are attracted to the anode. When a copper ion touches the cathode, it acquires two electrons from that electrode and becomes a copper atom. In a short time a freshly deposited layer of copper can be seen on the electrode. As often as a copper ion takes two electrons from the cathode, two chloride ions give two electrons to the anode. A chloride ion minus an electron is a chlorine atom. These atoms combine in pairs to form chlorine gas, Cl_2 , which is given off at the anode. The electrons which are deposited on the anode pass through the wire and bulb back to the battery, where they are sent again to the cathode.

We see that electrons are not actually carried through the solution as they are through a metallic conductor, but the result in the outside circuit is exactly the same as if they were. When

electrons pass through a metallic conductor, no chemical reaction takes place, but a chemical reaction actually takes place in the solution of an electrolyte. We say that the solution has been *electrolyzed*. The reaction involved in the electrolysis of copper chloride is represented by the equation:



The copper chloride is decomposed into its elements, copper and chlorine. It must be borne in mind that the electric current is not responsible for the existence of the ions themselves in a solution. The ions were formed when the compound was originally produced from the elements of which it is composed.

A solution of sugar does not cause an electric current to pass through the wire and lamp filament because sugar is not ionized in water solution. We learned that carbon compounds have a tendency to share electrons almost equally with other atoms. Such substances do not separate into ions in water solution, but remain in the form of neutral molecules. This accounts for the absence of light when the apparatus described above is used for testing solutions of sugar, alcohol, glucose, and starch.

Strong and weak electrolytes. Arrhenius assumed that in any solution of an electrolyte there are molecules of unionized solute as well as ions. Incomplete electrolytic dissociation would explain why the lowering of the vapor pressure of a solution of an electrolyte like sodium chloride is not exactly twice that of a solution of a nonelectrolyte of the same molar concentration. Later, Debye and Hückel made a different explanation of this phenomenon, and their theory is now accepted. They agreed with Arrhenius that substances like those which gave a dim light when the electric current is passed through their solutions (weak electrolytes) exist largely in the molecular form. The relatively few molecules which are dissociated into ions supply so few ions to the solution that they cannot take electrons from one electrode and supply them to the other with sufficient speed to maintain a rapid flow of electrons through the wire. Acetic acid, ammonium hydroxide, and butyric acid exist largely in the form of molecules when in water solution. But in solutions of substances like those which give a bright light when electrolyzed (strong electrolytes) Debye and Hückel assume complete dissociation of the solutes into ions. In moderately dilute solutions of these ions there exists a certain amount of electrical attraction which is not great enough to pull the ions together to form neutral molecules, but is sufficient to prevent the ions from acting as if they were entirely independent of each other. In a solution of moderate concentration these

interionic attractions restrict the motion of individual ions to some extent, making it appear that there are fewer ions in the solution than are actually present. Thus the freezing-point depression and the boiling-point elevation are somewhat less than the value which might be expected from the number of ions present. We should expect these discrepancies to disappear in very dilute solutions, as actually they do. In very dilute solutions the ions are far enough apart to be completely independent of each other.

What happens when a dilute solution of sodium chloride is slowly evaporated? As water is removed, the ions are brought closer and closer together, each positive ion being surrounded by negative ions, and each negative ion attracting to itself positive ions. Eventually the ions will be separated by distances equal to those between the atoms in a crystal of sodium chloride, and the solid crystals form.

Dissociation of some strong electrolytes. The table below shows the ions which exist in a number of strong electrolytes. All soluble salts are entirely ionized. The bases of Groups I and II of the Periodic Table fall in this group.

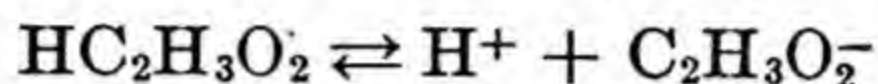
IONS OF A FEW STRONG ELECTROLYTES

<i>Compound</i>	<i>Ions</i>	
NaCl	Na ⁺	Cl ⁻
CuCl ₂	Cu ⁺⁺	2Cl ⁻
NaNO ₃	Na ⁺	NO ₃ ⁻
Na ₂ CO ₃	2Na ⁺	CO ₃ ⁻⁻
Na ₂ SO ₄	2Na ⁺	SO ₄ ⁻⁻
KHCO ₃	K ⁺	HCO ₃ ⁻
NaOH	Na ⁺	OH ⁻
KOH	K ⁺	OH ⁻
LiOH	Li ⁺	OH ⁻
Ca(OH) ₂	Ca ⁺⁺	2OH ⁻
Ba(OH) ₂	Ba ⁺⁺	2OH ⁻

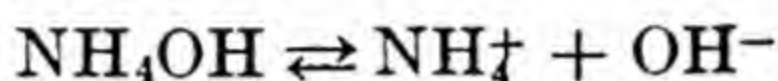
Ionization of strong acids. When we electrolyze a solution of hydrochloric acid with a light bulb inserted in the circuit, as described on page 215, we find that a bright light results from the passage of electrons. However, experimental evidence points to the conclusion that dry hydrogen chloride is a covalent compound. The hydrogen compounds of all of the halogens show a very low conductivity of electricity when in the liquid state but free from water. A water solution of hydrogen chloride, on the other hand, is an excellent conductor of electricity, and the solute must be highly ionized.

Ionization of weak electrolytes. Acetic acid, HC₂H₃O₂, exists for the most part as undissociated, neutral molecules. A few do break up into hydrogen and acetate ions, but whenever these come into contact with each other, they combine again to form a

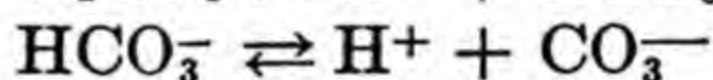
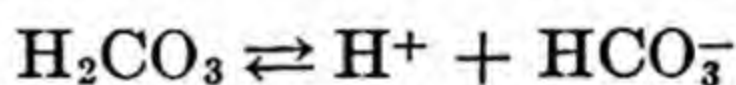
molecule of acetic acid, whereupon another molecule of acetic acid dissociates. There is always a definite concentration of ions present in a solution of acetic acid of given molality at any temperature. The percentage of ionization is greater the more dilute the solution. A solution of acetic acid containing 0.1 mole of acid per liter is about 1.3 per cent dissociated into ions. The ionization of acetic acid is indicated by the following equation:



The arrows pointing in both directions indicate that the ions and undissociated molecules are in equilibrium. Similarly, the partial ionization of ammonium hydroxide, NH_4OH , may be represented by the equation:

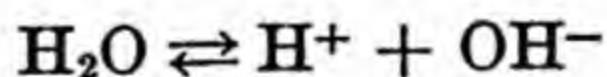


Carbonic acid, H_2CO_3 , ionizes in two steps:



A solution of carbonic acid containing 0.1 mole of carbonic acid per liter is only about 0.17 per cent ionized.

The ionization of water. Pure water is a very poor conductor of an electric current. In the experiment described on page 214 the bulb shows no light at all when the electrodes are placed in pure water. Other experimental evidence, however, indicates that some water molecules are dissociated into hydrogen and hydroxide ions. In 1 liter of water there is approximately 0.0000001 or 10^{-7} mole of hydrogen ions. Since water is a neutral substance, there must also be 10^{-7} mole of hydroxide ions. These ions are in equilibrium with molecular water, as indicated by the following equation:



When a hydrogen ion collides with a hydroxide ion, the two may combine to form a molecule of water. If this combination occurs, another molecule of water dissociates into ions, keeping the concentration of the ions constant at any temperature. In water the product of the concentrations of H^+ ions and OH^- ions is a constant quantity. The concentrations of ions in moles per liter are usually designated by their formulas enclosed in parentheses:

$$(\text{H}^+)(\text{OH}^-) = (1 \times 10^{-7})(1 \times 10^{-7}) = 1 \times 10^{-14}$$

This relationship holds whenever a solution contains both H^+ and OH^- . For example, there are hydroxide ions in an acid

solution, but fewer than there are in pure water. Let us calculate the concentration of OH^- in a solution which contains 0.1 mole of hydrochloric acid per liter of solution. Substituting in our formula the known concentration of H^+ and solving for (OH^-) we have

$$\begin{aligned} (0.1)(\text{OH}^-) &= 1 \times 10^{-14} \\ (\text{OH}^-) &= \frac{1 \times 10^{-14}}{0.1} = 1 \times 10^{-13}. \end{aligned}$$

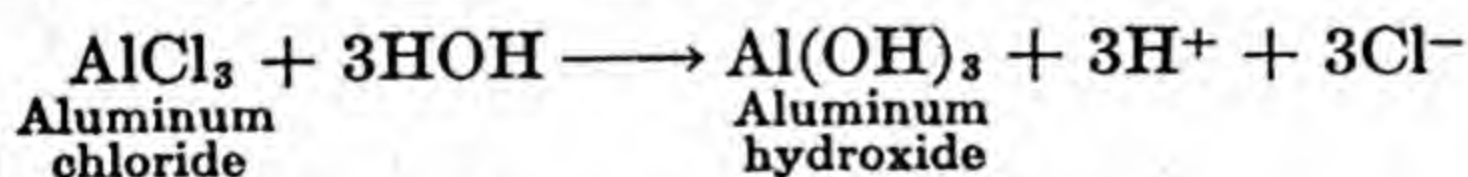
We see that there is 0.000000000000001 of a mole of hydroxide ion in each liter of a solution containing 0.1 mole of hydrochloric acid.

There are also hydrogen ions present in the solution of a base. We may calculate the concentration of hydrogen ions present in, for example, a solution containing 0.001 mole of sodium hydroxide, which is also 0.001 mole of OH^- per liter of solution.

$$\begin{aligned} (\text{H}^+)(\text{OH}^-) &= 1 \times 10^{-14} \\ (\text{H}^+)(1 \times 10^{-3}) &= 1 \times 10^{-14} \\ (\text{H}^+) &= \frac{1 \times 10^{-14}}{1 \times 10^{-3}} = 1 \times 10^{-11} \end{aligned}$$

This is actually 0.000000000000001 mole of hydrogen ions in a solution of a strong base which also contains 0.001 mole per liter of hydroxide ions.

A general definition for acids and bases. An acid may be defined as a compound which, in the presence of water, yields hydrogen ions, and a base is a compound which yields hydroxide ions. The fact that the solvent enters into the ionization of an acid or a base has led to the more general view that a compound which does not contain hydrogen is an acid if it removes hydroxide ions from water and leaves an excess of hydrogen ions in solution. Aluminum chloride, for example, contains no hydrogen, but if it is placed in water hydrogen ions are formed:

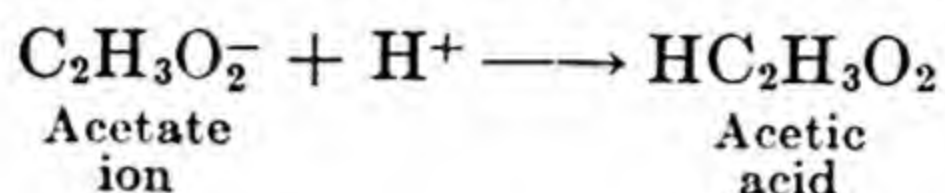


The aluminum hydroxide is insoluble and it removes hydroxide ions, leaving an acidic solution. Similarly a base may be defined as any compound which can remove hydrogen ions from water. Ammonia, NH_3 , is a base although it has no hydroxyl group. It can remove hydrogen ions from water, leaving hydroxyl groups in the solution:



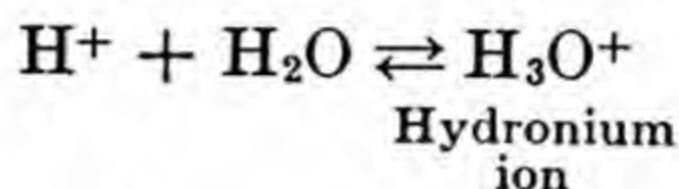
It has usually been said that ammonia and water combine to form ammonium hydroxide, NH_4OH , which then dissociates to some

extent, yielding hydroxide ions. The newer view is that the formation of NH_4OH is not a necessary intermediate step. The NH_3 takes a hydrogen ion from water forming NH_4^+ and somewhere in the solution an OH^- group is left without a partner. This view was developed by Bronsted several years ago. According to this system acetate ion must be a base since it combines with the hydrogen ion, or proton, to form the weak acid, acetic acid.

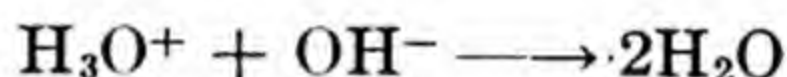


The hydroxyl group, OH^- , is a very strong base.

Water combines with hydrogen ions forming hydronium ions:

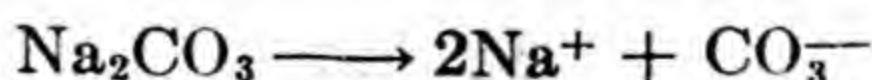


In any aqueous solution of an acid most of the hydrogen ions are present in this form. The reaction between a hydronium ion and a hydroxide ion is written:

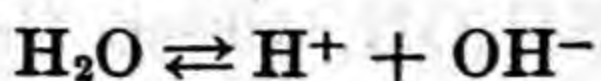


All positive ions combine with water to some extent but these *hydrated* ions act as if they were free and it is simpler to use a symbol like H^+ than to include a molecule of water and write it H_3O^+ . Many ions become associated with more than one molecule of water and it would be very cumbersome to write their symbols in the hydrated forms.

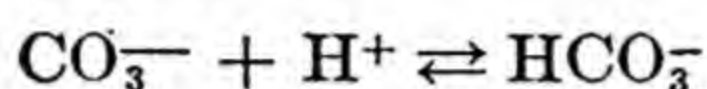
Hydrolysis. We are accustomed to thinking of a salt as a neutral substance. However, when we dissolve certain salts in water, and then test the solutions with litmus paper, we find that some of these salts show an alkaline reaction to litmus, and some others show an acid reaction. When, for example, a thoroughly purified sample of sodium carbonate is dissolved in water, we should expect the solution to contain only sodium ions and carbonate ions:



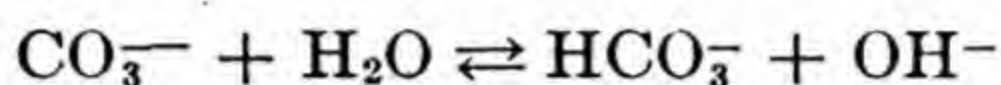
If, however, such a solution is tested with litmus paper, we find that it has an alkaline reaction. We have learned that only the presence of hydroxide ions (OH^-) causes such a change in the indicator. From what source, then, have the hydroxide ions come? Pure water contains a few hydrogen ions and hydroxide ions due to the ionization of some of the water molecules.



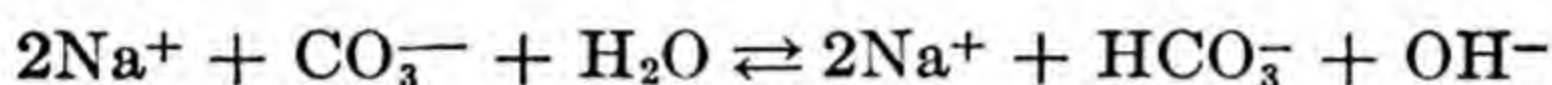
A solution of sodium carbonate owes its alkaline reaction to the hydroxide ions of the water making up the solution. Sodium carbonate is the salt formed by neutralizing the *strong base*, sodium hydroxide, with the *weak acid*, carbonic. You will recall that a weak acid prefers to remain, to a great extent, in the molecular form when in solution. Thus, when the carbonate ions from the sodium carbonate meet hydrogen ions from the water, they combine to form bicarbonate ions:



Another way to represent the hydrolysis would be:

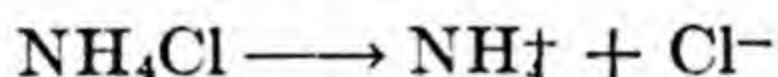


Or, more completely:

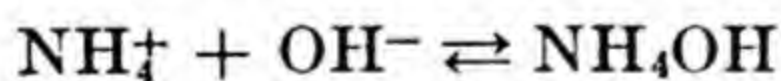


The free hydroxide ions in the solution color litmus blue. Carbonate ions remove the hydrogen ions from the solution, and free hydroxide ions are left unattached. These ions make the carbonate solution act like a base.

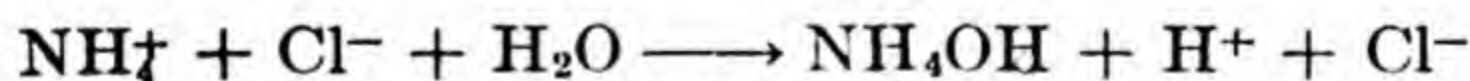
Again, if a solution of ammonium chloride, NH_4Cl , is tested with litmus, an acid reaction is noted. Ammonium chloride is the salt formed when ammonium hydroxide, a *weak base*, neutralizes hydrochloric acid, a *strong acid*. Water yields a few hydrogen ions and hydroxide ions as shown above, and ammonium chloride ionizes almost completely:



Ammonium ions combine with the hydroxide ions from the water, forming the weak (slightly ionized) ammonium hydroxide:



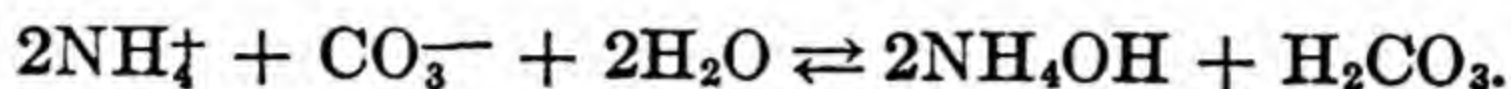
Or, more completely:



The hydrogen ions derived from the water remain in the solution unattached. The solution has, therefore, the properties of an acid.

On the other hand, when a salt like sodium chloride (the product formed when a *strong base* and a *strong acid* neutralize each other) is dissolved in water, the solution is neutral to litmus. There is no tendency either for the sodium ions to remove OH^- from the water, or for the chloride ions to remove H^+ from the water. Therefore, the same number of hydrogen and hydroxide ions remain, and the solution is neutral.

If both the base and the acid which form the salt are weak, both hydrogen ions and hydroxide ions are removed. A solution of ammonium carbonate illustrates this behavior:



Such a solution remains practically neutral.

All cases in which the ions of a salt combine with the hydrogen ions or the hydroxide ions of water are examples of *hydrolysis*. The equations show that hydrolysis is the reversal of the neutralization process.

Questions and Exercises

1. Name three classes of compounds that dissociate into ions when dissolved in water.
2. Do atoms of metallic elements lose or gain electrons when they become positive ions?
3. Do atoms of nonmetals lose or gain electrons when they become negative ions?
4. What is meant by the term *electrolyte*?
5. What is meant by the term *nonelectrolyte*?
6. Is the freezing point of a solution higher or lower than the freezing point of a pure solvent?
7. Is the lowering of the freezing point proportional to the number of dissolved particles?
8. Is an ion as effective as an undissociated molecule in lowering the freezing point of a solvent?
9. Write an equation showing what happens when sodium chloride dissolves in water.
10. Make as complete a distinction as you can between a sodium atom and a sodium ion.
11. Write the formulas of the ions formed when the following substances dissolve in water:

(a) NaNO_3	(d) K_2SO_4	(g) $(\text{NH}_4)_2\text{SO}_4$	(j) KCl
(b) HCl	(e) NaOH	(h) Li_2CO_3	(k) $\text{Ca}(\text{NO}_3)_2$
(c) Na_3PO_4	(f) KNO_3	(i) $\text{Mg}(\text{OH})_2$	(l) MgSO_4

12. Write the formulas for all the compounds that can be made from the following ions: Na^+ , Ca^{++} , H^+ , K^+ , NO_3^- , Cl^- , SO_4^{--} , and OH^- .

13. Copper sulfate is blue, copper chloride is green, and copper iodide is brown. Account for the fact that dilute solutions of these three salts have the same color (blue). (What ion is present in each of the three solutions?)

14. Dilute solutions of all acids have a sour taste, and all such solutions turn blue litmus red. To what common constituent in the acid solutions can you ascribe these properties?

15. Why does a body of salt water sometimes remain free from ice when a fresh-water lake in the same vicinity is frozen over?

16. Distinguish between a hydrogen molecule, a hydrogen atom, and a hydrogen ion. Write a symbol or formula for each.

17. Name several properties of (a) the chlorine atom; (b) the chloride ion.

18. Define (a) dissociation; (b) ion; (c) weak electrolyte.

19. Define in terms of ions (a) an acid; (b) a base; (c) a salt.

20. Upon what does the strength of an acid or a base depend?

21. Name (a) a strong acid; (b) a strong base; (c) a weak base; (d) a weak acid.

22. Explain in terms of ions the action on litmus of a water solution of (a) HCl; (b) KOH; (c) KCl.

23. Calculate the concentration (moles per liter) of hydrogen ions present in a solution of potassium hydroxide which contains (a) 1 mole of OH^- per liter; (b) 0.5 mole of OH^- per liter; (c) 0.005 mole of OH^- per liter.

24. Calculate the concentration (moles per liter) of hydroxide ions present in a solution of sulfuric acid which contains (a) 1 mole of H_2SO_4 per liter; (b) 0.0000001 mole of H_2SO_4 per liter.

25. Define hydrolysis.

26. Which of the following salts hydrolyze in water solution? Write all equations involved.

(a) K_2SO_4

(d) KCl

(g) $\text{NaC}_2\text{H}_3\text{O}_2$

(j) Na_2SO_4

(b) CuSO_4

(e) NaNO_3

(h) LiCl

(k) NaHCO_3

(c) ZnCl_2

(f) $\text{Al}_2(\text{SO}_4)_3$

(i) K_2CO_3

(l) NH_4HCO_3

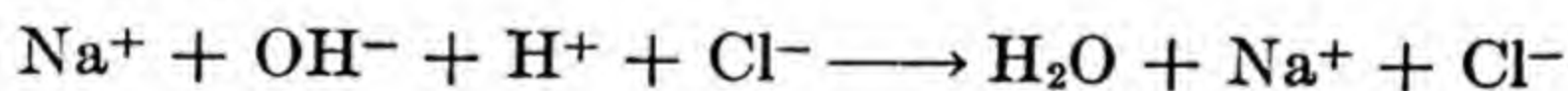
PART 3

Equations for Reactions Involving Ions

We have learned that a chemical equation is a statement of what takes place during a chemical reaction. If, then, the reaction involves water solutions of strong electrolytes, either as reactants or as products of the reaction, these electrolytes should be written in the form of their ions, since they actually exist as such in the solution.

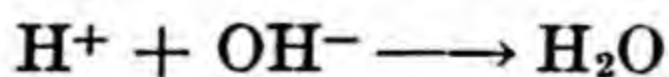
For example, let us consider the neutralization of hydrochloric acid with a solution of sodium hydroxide. Hydrochloric acid is a strong acid; that is, it exists in water solution in the dissociated form, or as hydrogen ions, H^+ , and chloride ions, Cl^- . Sodium hydroxide is a strong base, and in solution it exists in the form of sodium ions, Na^+ , and hydroxide ions, OH^- .

When hydrochloric acid is added to a sodium hydroxide solution, the equation for the process of neutralization should be written as follows:



We know that water does not conduct an electric current, and is not dissociated into ions to an appreciable extent. There are actually present in pure water a few hydrogen ions and hydroxide ions, but most of the water is in the form of undissociated molecules. Water, therefore, is represented by its formula, H_2O .

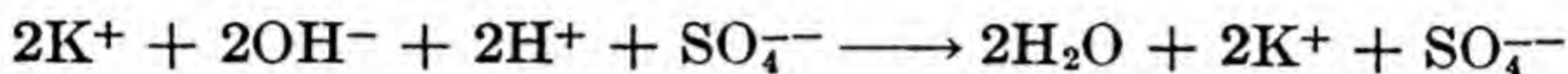
Sodium chloride, like all other soluble salts which we commonly use in the laboratory, is a strong electrolyte. It exists, in a water solution, in the form of ions. We see from the equation that the only reaction which takes place when hydrochloric acid is neutralized by sodium hydroxide is the union of hydrogen ions and hydroxide ions to form water:



The sodium ions and chloride ions are unchanged during the neutralization process. They existed as ions in the original solutions, and they are ions at the end of the reaction. If the water is evaporated from the solution after neutralization, solid

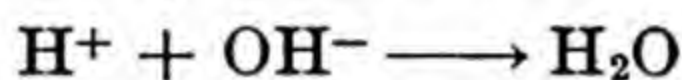
sodium chloride is obtained, but so doing involves a second reaction; namely, the vaporization of the water present, and the combination of the ions of salt to form the crystal lattice of sodium chloride.

Let us consider the reaction between potassium hydroxide and sulfuric acid, both strong electrolytes. Potassium hydroxide, a strong base, should be written in the form of its ions, K^+ and OH^- , since it exists in this form in solution. Sulfuric acid, a strong acid, exists in water solution as its ions, hydrogen ions and sulfate ions. When these two solutions are mixed in the proper amounts so that the hydrogen ions neutralize the hydroxide ions, the equation for the reaction is as follows:



Compare this equation with the one written on page 211.

Once again we see that the reaction merely involves the combination of hydrogen and hydroxide ions to form water:



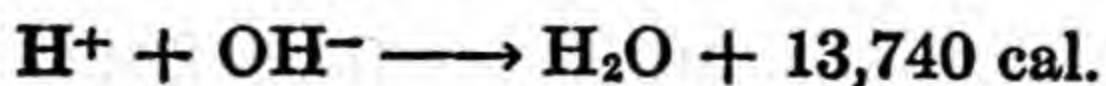
Potassium sulfate is a soluble salt, and its ions have no tendency to combine in water solution. The salt is obtained only when evaporation of the water from the solution has taken place.

It is a simple matter to prove experimentally that the reaction between a strong acid and a strong base involves only the combination of hydrogen and hydroxide ions. Accompanying every chemical reaction is a definite change in energy. Some reactions give out heat, others absorb heat, but for any specific reaction this change in energy has a definite value. It is a property of the reaction. In addition, no two chemical reactions have exactly the same change in heat content.

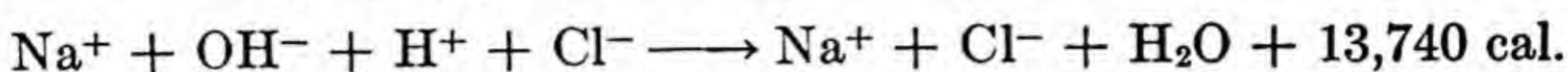
The quantities of heat liberated during the neutralization of many acids with different bases have been measured. Some of the results are as follows:



It is seen that the heat liberated when one mole of water is formed is the same, irrespective of the strong acid or strong base used in the neutralization. This identical production of heat could occur only if the acids and bases used in the various neutralization processes were already in the form of ions, and if the only reaction involved is the formation of water. We may therefore write:

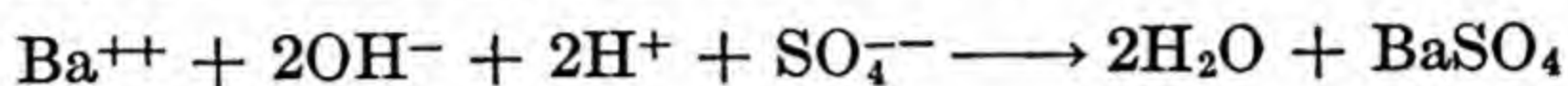


The compounds appearing in the three equations above should, therefore, be represented as completely ionized. The first equation, for example, may be written as follows:



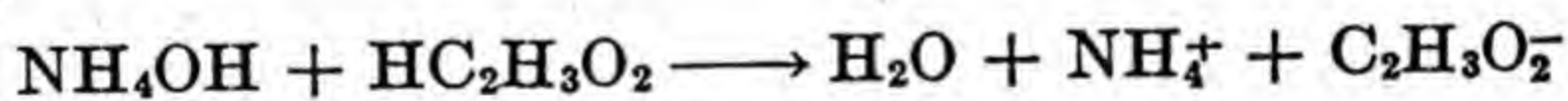
This form indicates that nothing has happened except the union of H^+ and OH^- to form H_2O .

When sulfuric acid is neutralized by barium hydroxide, a strong base, the following reaction occurs:



Barium sulfate is an *insoluble* salt, and it forms a precipitate during the neutralization process. Since it actually exists in the form of insoluble barium sulfate molecules at the end of the reaction, the formula for barium sulfate molecules, instead of the ions of the salt, should be used in the equation. The amount of heat given off by this reaction is not 13,740 cal. since a second reaction has taken place at the same time, namely, the combination of Ba^{++} and SO_4^{--} to form insoluble BaSO_4 . This reaction has its own energy change. Hence the measured heat of reaction is the result of these two simultaneous reactions.

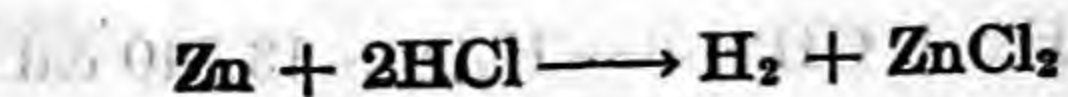
Weak electrolytes exist largely as undissociated molecules when dissolved in water. Since the greater part of a weak electrolyte is un-ionized, such a substance should be represented in an equation by its formula instead of by its ions. If, for instance, we write the equation for the neutralization of acetic acid, a weak acid, with ammonium hydroxide, a weak base, the reaction is expressed by the equation:



Ammonium acetate is a soluble salt; hence it exists in the form of its ions and is written in this way in the equation. The heat evolved by this reaction is less than 13,740 cal. This may be because some of the heat energy is absorbed in the continued ionization of the molecules of the weak acid and weak base to supply H^+ and OH^- which then neutralize each other.

We have written, in earlier chapters, many equations in which strong acids, strong bases, and soluble salts appeared. Let us rewrite some of these, showing the presence of ions where these occur.

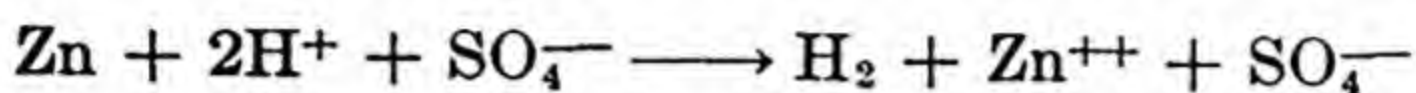
Hydrogen is formed by the action of a metal on an acid. We represented the reaction between zinc and hydrochloric acid by the equation:



Since hydrochloric acid is a strong acid, and zinc chloride is a soluble salt, the reaction should be written as follows:

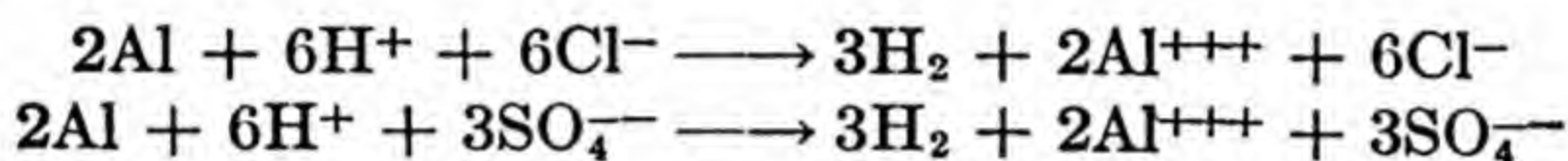


Similarly, the reaction between zinc and sulfuric acid is written:



Hydrogen gas is produced by the reaction of an acid on a metal, the metal taking the place of the hydrogen ions in the solution. Neither zinc nor iron will react readily with *concentrated* sulfuric acid. The undissociated acid reacts very slowly with a metal. Concentrated sulfuric acid is actually shipped in iron drums for commercial purposes.

Aluminum likewise replaces hydrogen ions in a solution of hydrochloric or sulfuric acid:

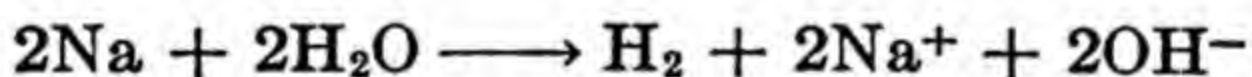


Compare these reactions with those on page 143.

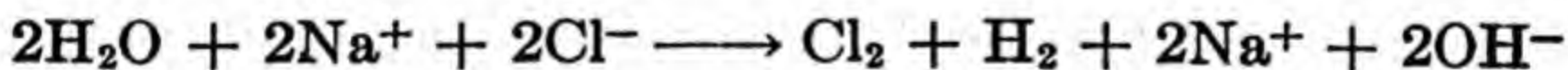
Hydrogen is prepared also by the reaction between metals and water. The reaction between sodium and water was written on page 54 as follows:



The ionic equation is written:



The equation for the formation of chlorine by the electrolysis of a solution of sodium chloride should be written as follows:



Sodium chloride is a soluble salt, and sodium hydroxide is a strong base.

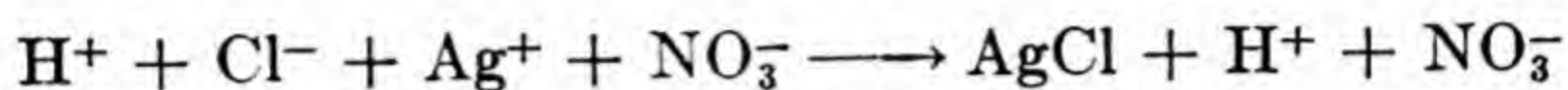
We must remember that concentrated sulfuric acid is not dissociated into hydrogen ions and sulfate ions, as it is in a dilute aqueous solution of the acid. It exists largely in the form of molecules. In the preparation of hydrogen chloride gas, concentrated sulfuric acid is added to solid sodium chloride, yielding hydrogen chloride gas and solid sodium sulfate. There is no water present, and the substances are all represented by their molecular formulas in the equation:



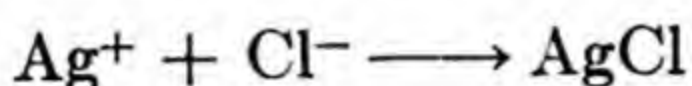
The test for a chloride is the formation of a white precipitate of silver chloride on the addition of a solution of silver nitrate to the solution in question. In the case of hydrochloric acid, the equation was written:



When ions are written where they occur, the equation becomes



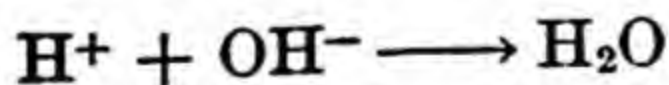
The only reaction which takes place is the combination of silver ions and chloride ions to form insoluble silver chloride:



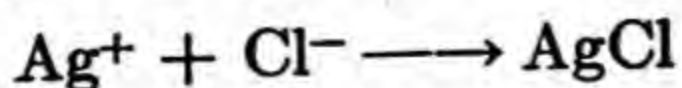
Any soluble silver salt may be used in the test for a chloride and, in the presence of any soluble chloride, will give a precipitate of silver chloride. This, therefore, is a test for *chloride ions*, and not for chlorine atoms. If a soluble silver salt is added to a solution of potassium chlorate, KClO_3 , or to carbon tetrachloride, CCl_4 , no precipitate of silver chloride is formed, since neither of these substances yields chloride ions.

Other types of reactions which go to an end. We have learned that when one of the products of a reaction is a *gas*, which is removed from the field of action as fast as it is formed, the reaction goes to an end.

Similarly, the combination of ions in a solution to form *undissociated molecules* is a process which goes to an end. The reacting substances in this case are removed from the field of action almost as effectively as if they had been taken out of the reaction vessel. For example, during the neutralization of an acid with a base, hydrogen and hydroxide ions combine to form molecules of water. The ions are removed from the solution, to a great extent, by the formation of the inactive and undissociated water molecules:



When ions in a solution combine to form an *insoluble substance*, as in the combination of silver ions and chloride ions to form silver chloride, the reaction goes to completion:



The reaction between barium chloride and sodium sulfate, in aqueous solution, goes to an end because one of the products formed is insoluble and precipitates as fast as formed:



To summarize: Reactions go to completion when one of the products of the reaction is a gas, a precipitate, or water.

Questions and Exercises

Rewrite the following equations in ions, where ions occur. Unless otherwise specified, assume, in each case, that water is present:

1. $2\text{H}_2\text{O} \longrightarrow 2\text{H}_2 + \text{O}_2$
2. $2\text{K} + 2\text{H}_2\text{O} \longrightarrow \text{H}_2 + 2\text{KOH}$
3. $\text{Ca} + 2\text{H}_2\text{O} \longrightarrow \text{H}_2 + \text{Ca}(\text{OH})_2$
4. $2\text{KClO}_3 \text{ (solid)} \longrightarrow 2\text{KCl (solid)} + 3\text{O}_2$
5. $\text{Fe} + 2\text{HCl} \longrightarrow \text{H}_2 + \text{FeCl}_2$
6. $\text{Fe} + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2 + \text{FeSO}_4$
7. $\text{Mg} + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2 + \text{MgSO}_4$
8. $\text{CuO (dry)} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O}$
9. $2\text{Li} + 2\text{HCl} \longrightarrow \text{H}_2 + 2\text{LiCl}$
10. $\text{Fe}_3\text{O}_4 \text{ (dry)} + 4\text{H}_2 \longrightarrow 3\text{Fe} + 4\text{H}_2\text{O}$
11. $\text{AgNO}_3 + \text{NaCl} \longrightarrow \text{AgCl} + \text{NaNO}_3$
12. $2\text{Na} + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2 + \text{Na}_2\text{SO}_4$
13. $\text{Na}_2\text{O}_2 + 2\text{HCl} \longrightarrow \text{H}_2\text{O}_2 + 2\text{NaCl}$
14. $2\text{H}_2\text{O} + 2\text{KCl} \longrightarrow \text{Cl}_2 + \text{H}_2 + 2\text{KOH (electrolysis)}$
15. $2\text{Cs} + 2\text{H}_2\text{O} \longrightarrow \text{H}_2 + 2\text{CsOH}$
16. $2\text{HCl} \longrightarrow \text{H}_2 + \text{Cl}_2$
17. $4\text{HCl (conc.)} + \text{MnO}_2 \longrightarrow 2\text{H}_2\text{O} + \text{MnCl}_2 + \text{Cl}_2$
18. $\text{F}_2 + 2\text{NaCl} \longrightarrow \text{Cl}_2 + 2\text{NaF}$
19. $\text{Br}_2 + 2\text{HI} \longrightarrow \text{I}_2 + 2\text{HBr}$
20. $\text{MgO} + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{O} + \text{MgSO}_4$
21. $\text{LiOH} + \text{HNO}_3 \longrightarrow \text{H}_2\text{O} + \text{LiNO}_3$
22. $3\text{KOH} + \text{H}_3\text{PO}_4 \longrightarrow 3\text{H}_2\text{O} + \text{K}_3\text{PO}_4$
23. $3\text{HCl} + \text{Al}(\text{OH})_3 \longrightarrow 3\text{H}_2\text{O} + \text{AlCl}_3$
24. $3\text{H}_2\text{SO}_4 + 2\text{Fe}(\text{OH})_3 \longrightarrow 6\text{H}_2\text{O} + \text{Fe}_2(\text{SO}_4)_3$
25. $2\text{HCl} + \text{Pb}(\text{OH})_2 \longrightarrow 2\text{H}_2\text{O} + \text{PbCl}_2$
26. $\text{H}_2\text{SO}_4 + \text{Cu}(\text{OH})_2 \longrightarrow 2\text{H}_2\text{O} + \text{CuSO}_4$

PART 4

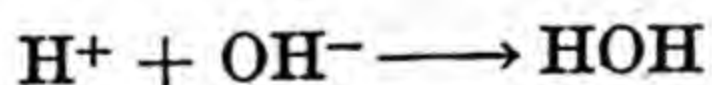
Standard Solutions; Titrations

A chemist is often called upon to determine the strength of a solution of an acid or base. He may, for example, want to know how much acetic acid there is in a quart of vinegar. He first makes what is known as a standard solution of a base, preferably sodium hydroxide. A *standard solution* is one of any definite, known concentration. He may dissolve one gram molecule, or mole (40 g.), of sodium hydroxide in water, and dilute the solution to 1 liter. Such a solution is called a one-molar solution.

A sample of vinegar of known volume is then placed in a beaker. It may or may not be diluted with water. A few drops of litmus are added to the solution in the beaker, and since vinegar contains hydrogen ions, the litmus immediately turns pink.

The standard sodium hydroxide solution is then added drop by drop from a burette, until the litmus changes from red to lavender. At this point the solution contains neither free hydrogen ions nor free hydroxide ions (see Neutralization, page 210).

When an acid and a base neutralize one another, the same number of hydrogen ions and hydroxide ions react:



That is, one hydrogen ion combines with one hydroxide ion, or a million hydrogen ions combine with a million hydroxide ions.

Since the sodium hydroxide solution was one of known strength, the number of OH ions which were added to the vinegar solution is known. This is also the number of hydrogen ions present in our sample.

Let us suppose that the sample of vinegar measured exactly 25 cc., and that it required 20 cc. of the one-molar base solution to neutralize it.

Since 1 liter of the base contains 1 mole of sodium hydroxide, then 20 cc. contain

$$\frac{20}{1000} \times 1 = 0.02 \text{ mole.}$$

This amount neutralized 25 cc. of vinegar. Hence there were present in the 25-cc. sample 0.02 mole of acetic acid. The acid and base react in equimolar amounts:



In a liter of this sample of vinegar, then, there are

$$\frac{1000}{25} \times 0.02 = 0.8 \text{ mole of acetic acid.}$$

The vinegar is said to be 0.8 molar with respect to acetic acid. The weight of acetic acid in a liter of this sample of vinegar is $0.8 \times 60 = 48$ g. A mole of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, weighs 60 g.

A solution containing a base, such as potassium hydroxide, may be analyzed in a similar manner. In this case a standard solution of an acid, preferably hydrochloric acid, is made.

Let us suppose that the standard acid solution contains $\frac{1}{10}$ or 0.1 mole of hydrochloric acid per liter (0.1M), and that it requires exactly 15 cc. of the acid to neutralize 20 cc. of the unknown solution of base. Since 1000 cc. of the acid solution contain 0.1 mole of HCl, 15 cc. contain

$$\frac{15}{1000} \times 0.1 = 0.0015 \text{ mole of HCl (or H}^+).$$

Then we know that the 20 cc. of the potassium hydroxide solution also contains 0.0015 moles of KOH. A liter of the solution contains

$$\frac{1000}{20} \times 0.0015 = 0.075 \text{ mole,}$$

and we say that the potassium hydroxide solution is 0.075 molar (or 0.075M). The molecular weight of potassium hydroxide is 56, and the 0.075 molar solution contains 0.075×56 or 4.2 g. of KOH per liter, or 0.0042 g. of KOH per cubic centimeter.

This process of neutralizing an acid or base with a measured volume of a standard solution is called *titration*.

Normal solutions. In the examples which we have given, one mole of acid neutralized one mole of base. In many chemical reactions, a mole of one compound reacts with two or three or

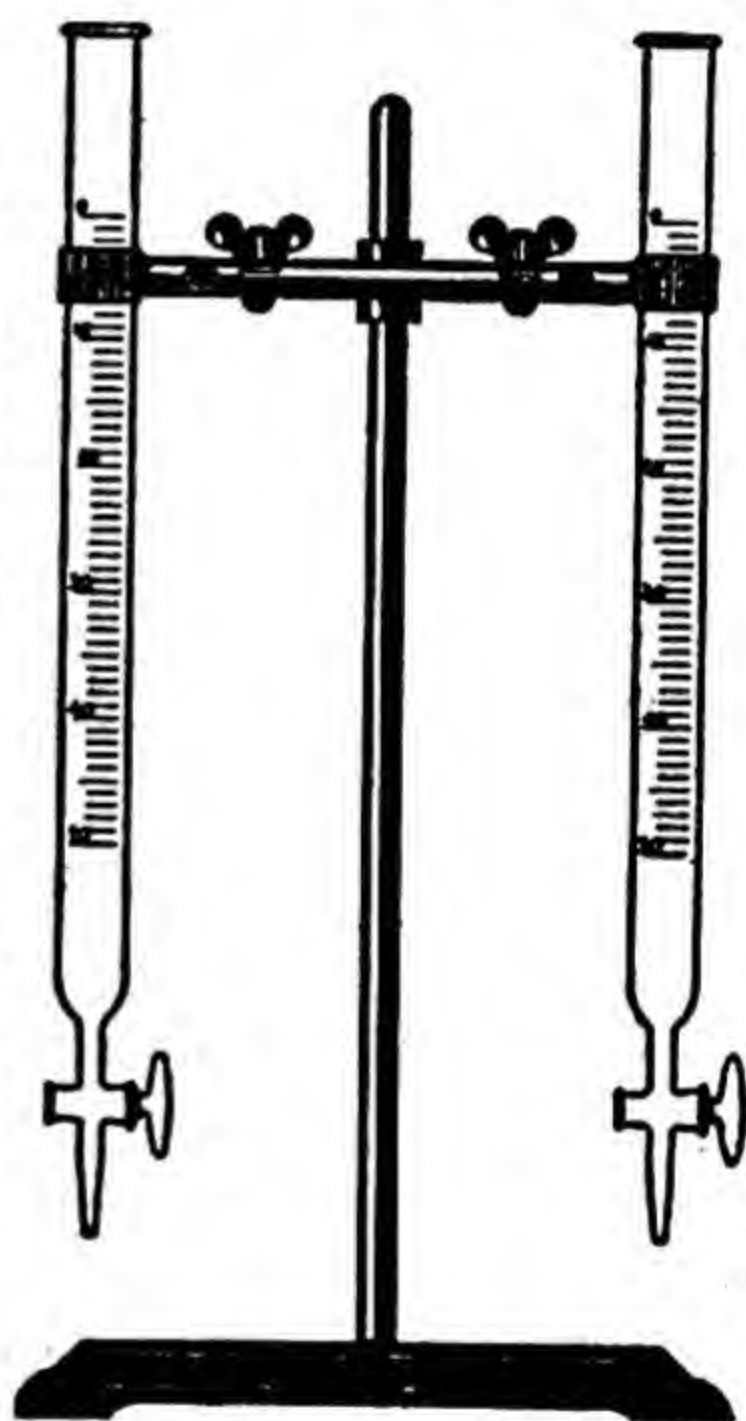


Fig. 121. Burettes are used for titration.

more moles of another substance. An example is the neutralization of sulfuric acid with sodium hydroxide:



Sulfuric acid yields two grams of hydrogen ions for every mole of acid and, therefore, requires two moles of sodium hydroxide for complete neutralization. One mole of sodium hydroxide is actually *equivalent* to one-half mole of sulfuric acid.

For this reason standard solutions are often made containing a known number of *equivalents*, rather than *moles*, of the reacting substance. An equivalent of any acid is the weight of that acid which contains 1 g. of replaceable hydrogen. A *normal* solution of an acid contains the *equivalent* weight of the acid in 1000 cc. of the solution. A *molar* solution of hydrochloric acid is also a *normal* solution, since it contains 1 g. of hydrogen ion. A molar solution of sulfuric acid, however, is a two-normal solution (2*N*), since it contains 2 g. of hydrogen ion. A one-normal (1*N*) solution of this acid would contain $\frac{9.8}{2} = 4.9$ g. of sulfuric acid per liter. Similarly, a normal (1*N*) solution of phosphoric acid (H_3PO_4) would contain $\frac{9.8}{3} = 3.266$ g. per liter, and a one-molar solution of this acid would be three-normal, since it contains 3 g. of replaceable hydrogen.

A normal solution of a base contains 17 g. of OH ion, since this is the weight which reacts with 1 g. of hydrogen ion. Forty grams of sodium hydroxide contained in 1 liter of solution is both a molar and a normal solution, for it contains 17 g. of hydroxide ion. One-molar calcium hydroxide, $\text{Ca}(\text{OH})_2$, is a two-normal solution, since it contains 2×17 g. of hydroxide ion per liter.

When titrations are performed with normal solutions, the calculations are made exactly as in the case of molar solutions, except that the results are reported in equivalents rather than in moles.

The pH of a solution. The concentration of hydrogen ions in a solution is often expressed in terms of pH rather than as moles per liter, or as equivalents per liter. This system of expressing hydrogen-ion concentration is illustrated by the following examples:

Let us make a solution of hydrochloric acid containing 0.1 mole of hydrogen chloride in 1 liter of solution. The solution is then 0.1 molar. Since we may consider hydrochloric acid entirely dissociated into its ions in dilute solution, the concentration of hydrogen ions is also 0.1 molar. We may write this value as 0.1, as $\frac{1}{10}$, or as 10^{-1} . The number 10 raised to the power

of -1 is written 10^{-1} , and it is equal to 0.1 . In other words, the *logarithm* of 0.1 is -1 . The logarithm of a number is the power to which 10 must be raised to make that number.

The *pH* of a solution is the logarithm of the concentration of hydrogen ions, in moles per liter, with the sign of the logarithm reversed. For example, the logarithm of 0.1 is -1 , and the *pH* of a $0.1M$ solution of hydrochloric acid is 1 .

Let us express hydrogen-ion concentrations of $0.01M$, $0.001M$, $0.0001M$, and $0.00001M$ solutions of an acid such as hydrochloric acid in terms of *pH*:

Concentration in moles per liter	Logarithm	<i>pH</i>
$0.01 = 10^{-2}$	-2	2
$0.001 = 10^{-3}$	-3	3
$0.0001 = 10^{-4}$	-4	4
$0.00001 = 10^{-5}$	-5	5

It can be seen that the *pH* increases as the hydrogen-ion concentration decreases. In pure water, the concentration of hydrogen ions is $0.0000001M$, or 10^{-7} . Hence the *pH* of pure water is 7 , and this is the neutral point in the *pH* system. Since pure water is neutral, the concentration of hydroxide ions must also be 10^{-7} .

When dealing with solutions of bases, it is customary to express the result in terms of *pH* rather than *pOH*, but either method is permissible. The following table will make this clear:

Concentration of OH^- in moles per liter	Logarithm	<i>pOH</i>	Concentration of H^+ in moles per liter	<i>pH</i>
$0.1 = 10^{-1}$	-1	1	10^{-13}	13
$0.001 = 10^{-3}$	-3	3	10^{-11}	11
$0.00001 = 10^{-5}$	-5	5	10^{-9}	9
$0.0000001 = 10^{-7}$	7	7	10^{-7}	7

The *pH* method of expressing hydrogen-ion concentration is used extensively in biological and physiological studies, for it is a convenient way of dealing with the very dilute solutions generally used in biological work. Most of the normal body fluids have a *pH* near that of water; that is, they are almost neutral. The gastric juice is an exception, having a *pH* of 2 .

When the pH of a solution is known, we can calculate the hydrogen ion concentration in terms of moles per liter (or equivalents per liter). If, for example, the pH of a solution is equal to 6, we know that the logarithm of the concentration is -6 . Hence the hydrogen-ion concentration is 10^{-6} or 0.000001 mole per liter.

Questions and Exercises

1. How many moles of hydrochloric acid are there in a 30-cc. sample of the acid if this volume is completely neutralized by 40 cc. of 0.1M sodium hydroxide?
2. How many moles of acetic acid are contained in 1 liter of vinegar if it requires 10 cc. of 0.5M sodium hydroxide to neutralize a 20-cc. sample of the vinegar?
3. How many equivalents of sulfuric acid are present in a 50-cc. sample if it requires 40 cc. of 1N sodium hydroxide for complete neutralization?
4. How many grams of sulfuric acid are there in 1 liter of 2N sulfuric acid solution?
5. How many grams of calcium hydroxide, $Ca(OH)_2$, are contained in 100 cc. of (a) a one-molar solution; (b) a one-normal solution?
6. If 25 cc. of a sulfuric acid solution are neutralized by 20 cc. of a 0.5N potassium hydroxide solution, how many equivalents of H_2SO_4 are there per liter of solution? How many moles of H_2SO_4 per liter?

PART 5

Colloids

Certain substances such as sugar and salt are soluble in water; other substances, such as sand and clay, are usually considered insoluble. When sugar is added to water, the molecules become separated from the crystal and are distributed uniformly throughout the solvent. They cannot be separated from the water molecules by filtration.

If, on the other hand, we throw some grains of sand into a beaker of water and stir the mixture thoroughly, the sand settles to the bottom of the beaker as soon as the stirring is discontinued, because it is heavier than water and insoluble. The water is left as clear as it was at the beginning of the process.

Now let us grind some clay into small particles, and stir these thoroughly into a beaker of water. In time the greater amount of the clay settles to the bottom of the solution, owing to its weight and insolubility. If the contents of the beaker are now filtered through ordinary filter paper, the clay which precipitated out remains on the filter paper. The liquid that passes through, however, is not perfectly clear. It is turbid, showing that some particles of clay passed through the pores of the filter paper. Moreover, on further standing, these particles do not settle out but remain suspended in the liquid. They are said to be in the *colloidal state*.

The Tyndall effect. When a beam of light is passed through this filtrate, its path may be clearly seen through the liquid. This phenomenon is called the *Tyndall effect*. A solution of sugar or salt, on the other hand, does not show the path of a similar beam of light, because the molecules of solute are too small to reflect light. The effect is similar to that observed when we pass a beam of sunlight through a darkened room containing particles of dust too small to be seen under ordinary conditions. The particles become visible because each one reflects light to the eye, making the particles noticeable.

The Brownian movement. If some of the colloidal suspension is placed on the slide of a microscope which has a beam of light

directed into the drop of liquid on the slide, the particles of clay can be seen. Such an instrument is called an *ultramicroscope*. Moreover, the particles of clay are seen to be dancing around in the liquid. Any particle, if closely watched, will be seen to move about erratically in a zigzag path, not continuously in one direction. This movement of colloidal particles is called the *Brownian movement*, after Robert Brown, the Scottish scientist who first observed it.

This phenomenon was not understood for some years. Now we believe that each particle is being bombarded by the molecules of the water or other liquid in which the colloidal particles are

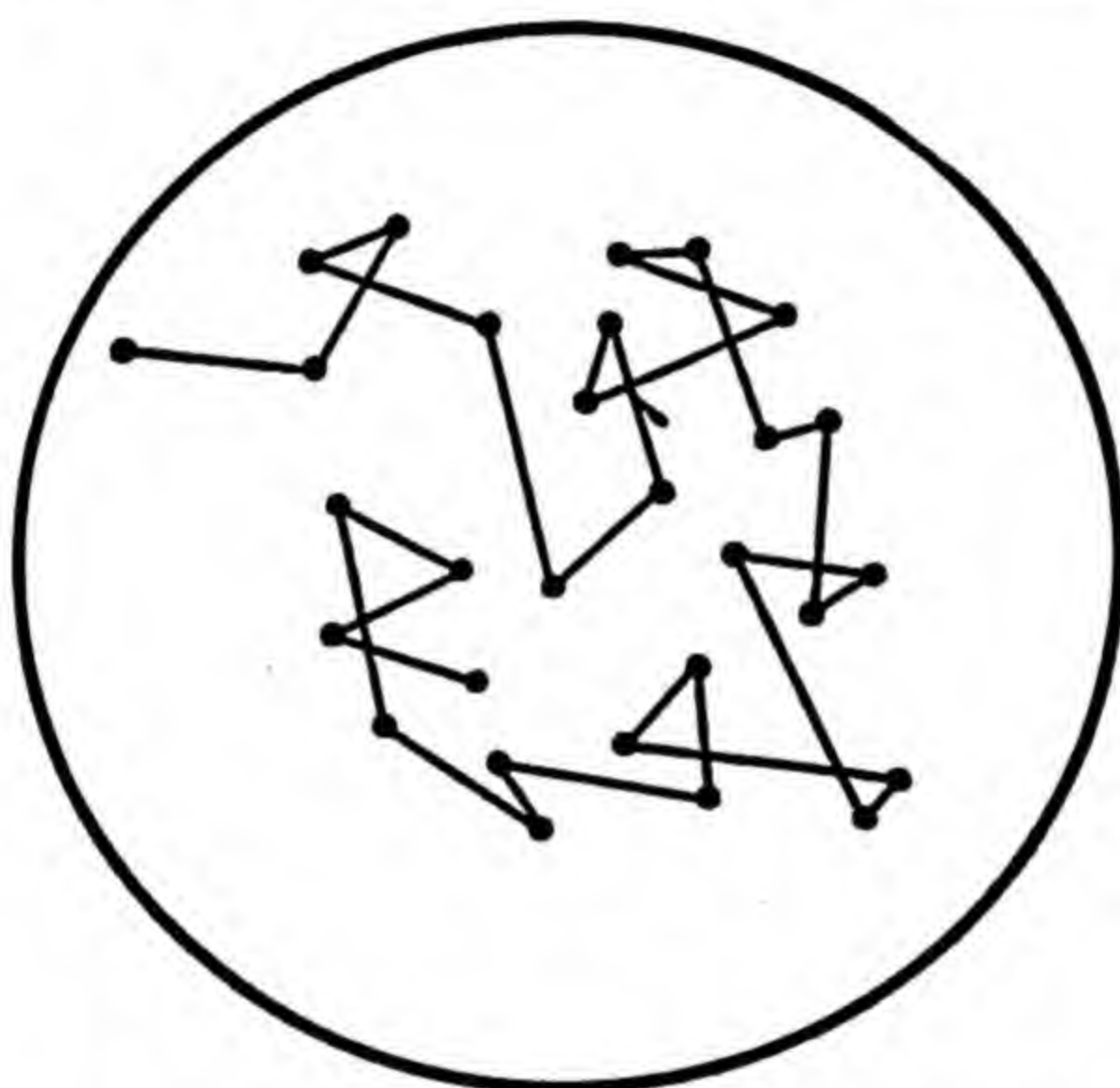


Fig. 122. Path of a colloidal particle. Brownian movement.

suspended. The molecules of a liquid or of a gas are in rapid motion. The molecules of water are too small to be seen even through the ultramicroscope, but the effect of their motion can easily be seen as we watch a colloidal particle. The particle is pushed in one direction and then in another, as rapidly moving water molecules bombard it.

This bombardment causes the particles to remain in suspension. In other words, the size of the particle determines whether it will disappear in solution, remain in suspension, or precipitate. If the particle is large enough to settle, regardless of the continuous blows from solvent molecules, it forms a precipitate at the bottom of the container. If it is of molecular size, it forms a true solution with the solvent. If it is too large to form a solution and too small to settle, it remains in suspension as a colloid. The solid is said to be dispersed in the liquid.

The size of the individual particles in a colloidal solution is so small that it is usually measured in millimicrons. One millimicron, $1\text{ m}\mu$, is one one-millionth of a millimeter. The smallest particle which can be seen with the aid of the most powerful microscope is about $100\text{ m}\mu$ in diameter, and this is about the size of the largest particles capable of forming a colloidal suspension or, as it is often called, a colloidal solution. The smallest colloidal particles are about $1\text{ m}\mu$ in diameter, and this is approximately the size of the largest molecules in solution. A colloidal particle, therefore, is between 0.0001 and 0.000001 mm. in diameter.

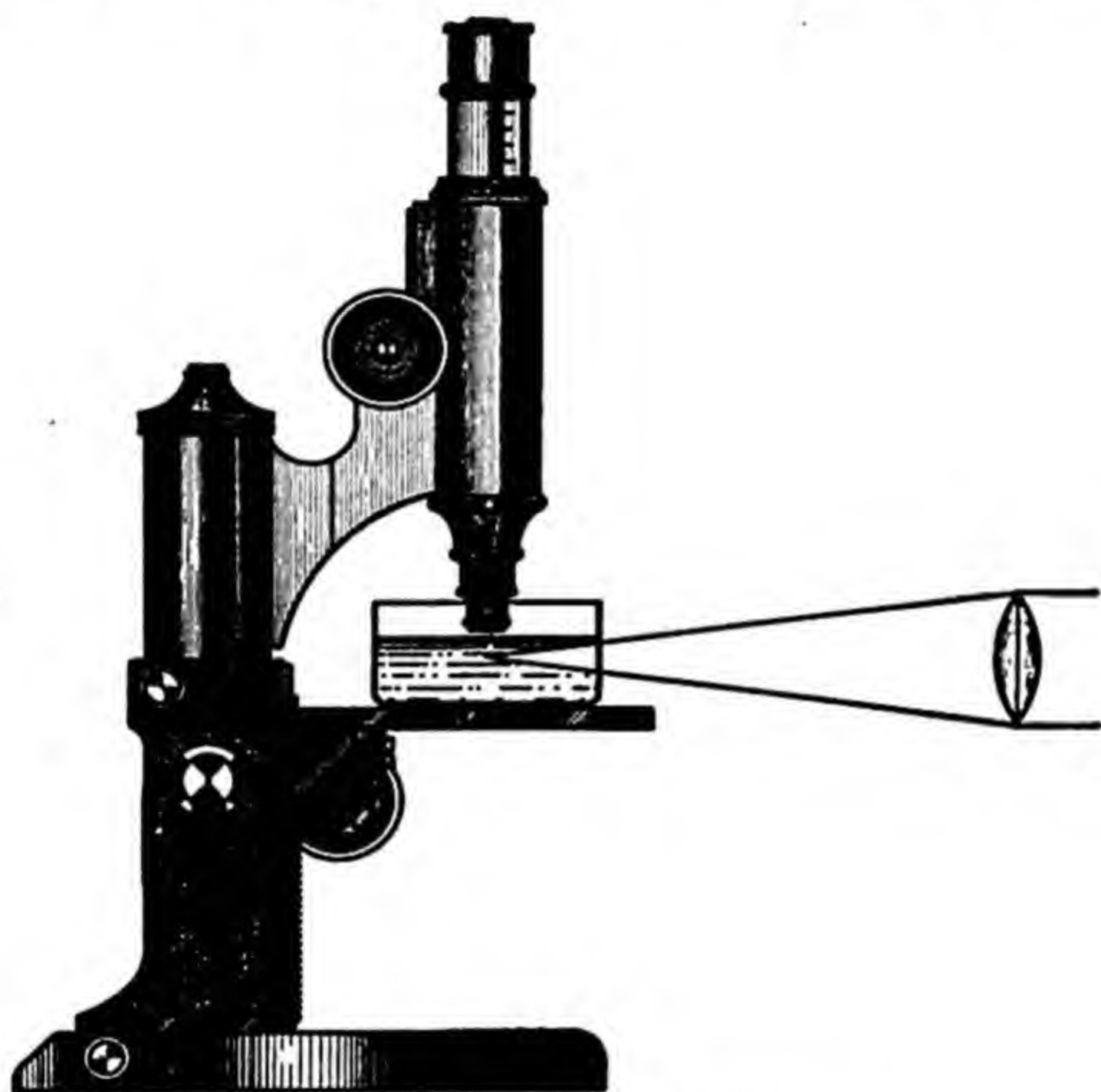
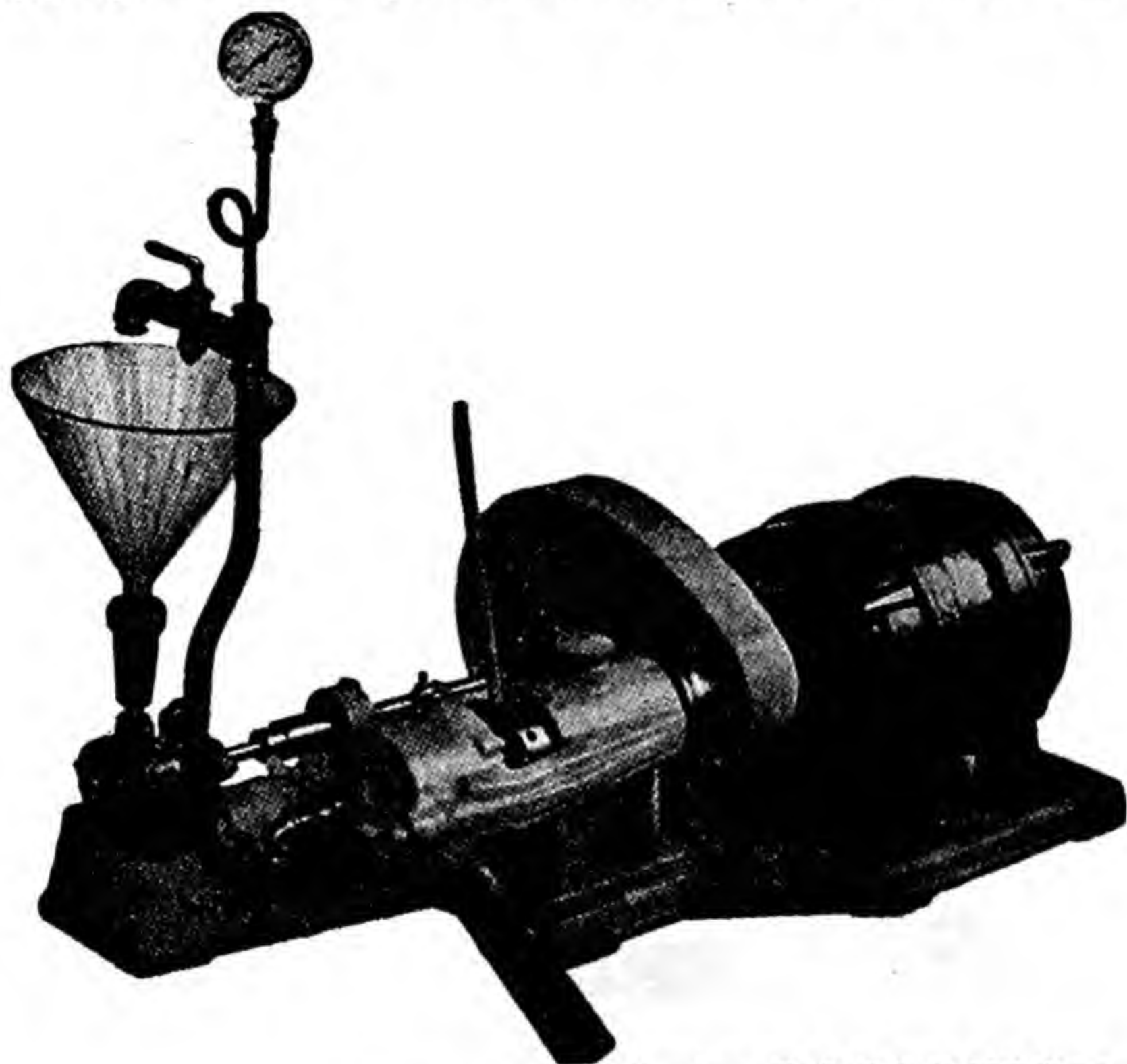


Fig. 123. The ultramicroscope.

Kinds of dispersed systems. Just as ordinary solutions may be composed of a gaseous, liquid, or solid solute in a gaseous, liquid, or solid solvent, so colloidal suspensions may consist of particles of a gas, solid, or liquid in some other medium. Colored glass and many colored precious stones, such as the ruby, sapphire, and amethyst, are examples of one solid dispersed in another. Ruby glass contains colloidal gold dispersed in the glass. Many metals may be dispersed in water. Red-gold suspensions in water have been kept for many years. Platinum is also easily dispersed in water. A cloud of dust or smoke illustrates the colloidal dispersion of a solid in a gas. A fruit like a pear or a viscous starch solution illustrates a liquid dispersed in a solid. If oil is shaken thoroughly with water, a colloidal suspension of a

liquid in a liquid results. The term emulsion is usually applied to this kind of system. Milk, jelly, mayonnaise, and butter are also examples of this type of colloid. A fog or mist consists of colloidal particles of liquid suspended in a gas. A gas dispersed in a liquid forms a foam. These are only a few of the many illustrations of colloids which might be given.

Preparation of colloids. There are two methods for making particle of colloidal size. The first of these we have already illustrated—that of *dispersion*, which consists in subdividing larger aggregates into particles of colloidal size. The second



Courtesy, U. S. Colloid Mill Corp.

Fig. 124. A colloid mill.

method, that of condensation, builds up particles of colloidal size from smaller ones, that is, from molecules or ions.

1. Dispersion methods. Grinding may be used to reduce the size of particles, but it is often difficult to obtain particles of sufficient fineness by this method. The colloid mill, which is illustrated in Fig. 124, is often used. It consists of two rapidly revolving surfaces, about 0.002 inch apart, between which particles in suspension are drawn. Such a mill is used also in preparing finely divided pigments for paints and printers' inks, and in preparing emulsions of various kinds.

Colloidal suspensions of gold, platinum, silver, and other metals have been formed by passing an arc between two wires

of the metal, held under water or other liquid. Particles of colloidal dimensions are separated from the wire and remain in suspension in the liquid.

Some solids disperse of their own accord when placed in the proper medium. The process is usually called peptization. Shellac, and some gums and resins, disperse in this way when immersed in alcohol.

Many colloids, most of which are of animal or vegetable origin, remain in suspension in water or other appropriate dispersing medium. These colloids include gelatin, glue, starch, tannins, soap, albumins, caramel, rubber, and nitrocotton. When in water, or other solvent, they form colloidal solutions or jellies very rapidly. They are called *lyophilic* colloids, which means "solvent-loving." When the solvent is water, they may be called *hydrophilic*, meaning "water-loving." The term *lyophobic* means "hater of the solvent," and *hydrophobic*, "water-hating." The colloidal metals are hydrophobic. Nitrocotton is lyophilic in a mixture of alcohol and ether, but lyophobic in water.

Many dispersed substances are in the form of threads which stretch through the solution forming a network, rather than in the form of droplets. These colloids are characterized by a high viscosity, and in more concentrated solutions, form jellies. Some of them contain both acidic and basic groups, and can unite with each other indefinitely and form a solid, jelly-like structure.

2. Condensation methods. These methods consist in preparing colloidal particles by chemical reaction between ions or molecules of substances. If special precautions are observed, precipitation can be avoided, and particles can be produced which are small enough to remain suspended in the liquid. Normally the treatment of arsenious ions with hydrogen sulfide forms a precipitate of arsenious sulfide, but if arsenious acid is acted upon by hydrogen sulfide in the absence of any considerable amount of electrolytes, a colloidal suspension of arsenious sulfide, As_2S_3 , is obtained. Such a suspension is bright yellow in color. A suspension of mercuric sulfide, HgS , can be prepared by the action of hydrogen sulfide on mercuric cyanide, $\text{Hg}(\text{CN})_2$. Both reactants are very weak electrolytes, and they furnish so few ions, that particles of colloidal dimensions are formed. Colloidal gold is prepared by the reduction of a very dilute solution of HAuCl_4 by means of an un-ionized reducing agent like formaldehyde.

Why colloids remain in suspension. What prevents several colloidal particles from forming a larger particle, one of sufficient size and weight to overcome the effect of the Brownian movement and precipitate from the solution?

It is found by experiment that most colloidal particles are electrically charged. Some carry negative charges; others are positively charged. In any one suspension, all the particles are charged in the same way. There seems to be a selective action by colloidal particles on ions of electrolytes found in the same solution. If no electrolytes are present, the ions of water may be differentially adsorbed. As a result they are able to migrate when an electric current is sent through the suspension, the direction being dependent upon the sign of charge which has been taken up by the colloid. This phenomenon is known as cataphoresis. It is thus possible to classify colloids as positive and negative. Particles of metals, metallic sulfides, clay, silicic acid, and graphite are examples of negative suspensions. Among the positive suspensions are metallic oxides, hydroxides, and many dyes. Since particles which have the same electric charge are repelled from each other, there is little tendency for two particles in the same suspension to combine to form a larger particle.

Colloidal particles surrounded by gelatin or some other gummy substance have difficulty in coming together and forming a sufficiently large aggregate to overcome the Brownian movement. Gelatin is sometimes added to other suspensions to prevent the formation of aggregates which might otherwise precipitate. Such an added colloid is called a *protective colloid*. Gelatin is added to ice cream for this purpose. It is added also to silver bromide in the manufacture of photographic plates in order to prevent the colloidal particles of silver bromide from coming together and forming particles large enough to precipitate from the solution.

The coagulation of colloids. Colloids may be coagulated by neutralizing the charges on the particles. The particles then increase in size and precipitate from the suspension.

Since colloids show a highly selective preference for either hydrogen ions or hydroxide ions, the addition of a dilute acid to a negative suspension—for example, arsenious sulfide—suffices to coagulate it. Similarly, the addition of a small amount of a base to a positive colloid—like ferric or aluminum hydroxide—coagulates it completely. In general, negative colloids may be coagulated by acids, and positive colloids by bases.

When milk sours, lactic acid is formed. The hydrogen ion from lactic acid neutralizes the negative charge on the suspended albumin and casein, causing them to precipitate in curds.

The formation of deltas and bars at the mouths of rivers is caused in the same way. We have learned that colloidal clay is negatively charged. These particles become suspended in large amounts as the river flows toward the sea. When sea water,

containing positively charged sodium and magnesium ions, comes in contact with the particles of clay, the charges on these particles are neutralized, and they coagulate into larger masses and settle out in the mouth of the river. This accumulation of clay forms the delta.

Adsorption. Solid surfaces have the power to adsorb gases. These gases form a layer one molecule thick on the surface. The lower the temperature the more slowly gas molecules move, and they are held more easily by the solid surface. The gases which are the most easily liquefied are also the ones which are most easily adsorbed by surfaces. Helium and hydrogen are the least adsorbed, while ammonia and water vapor are the most highly adsorbed. In the laboratory we heat a crucible to red heat, in order to remove the water vapor that is adhering to the surface, and then dry it in a desiccator before using it for quantitative work.

Colloids show this tendency to adsorb substances to a high degree, since for a given weight of the substance, particles in the colloidal state have an immense surface. For example, a cube having a length of 1 centimeter on each side has a total surface of 6 square centimeters. If it were divided into cubes which measured 0.0001 mm. on each edge, the total surface would be 600,000 sq. cm. It is clear that the smaller cubes with the greater total surface would be able to adsorb more molecules of another substance than the larger one could.

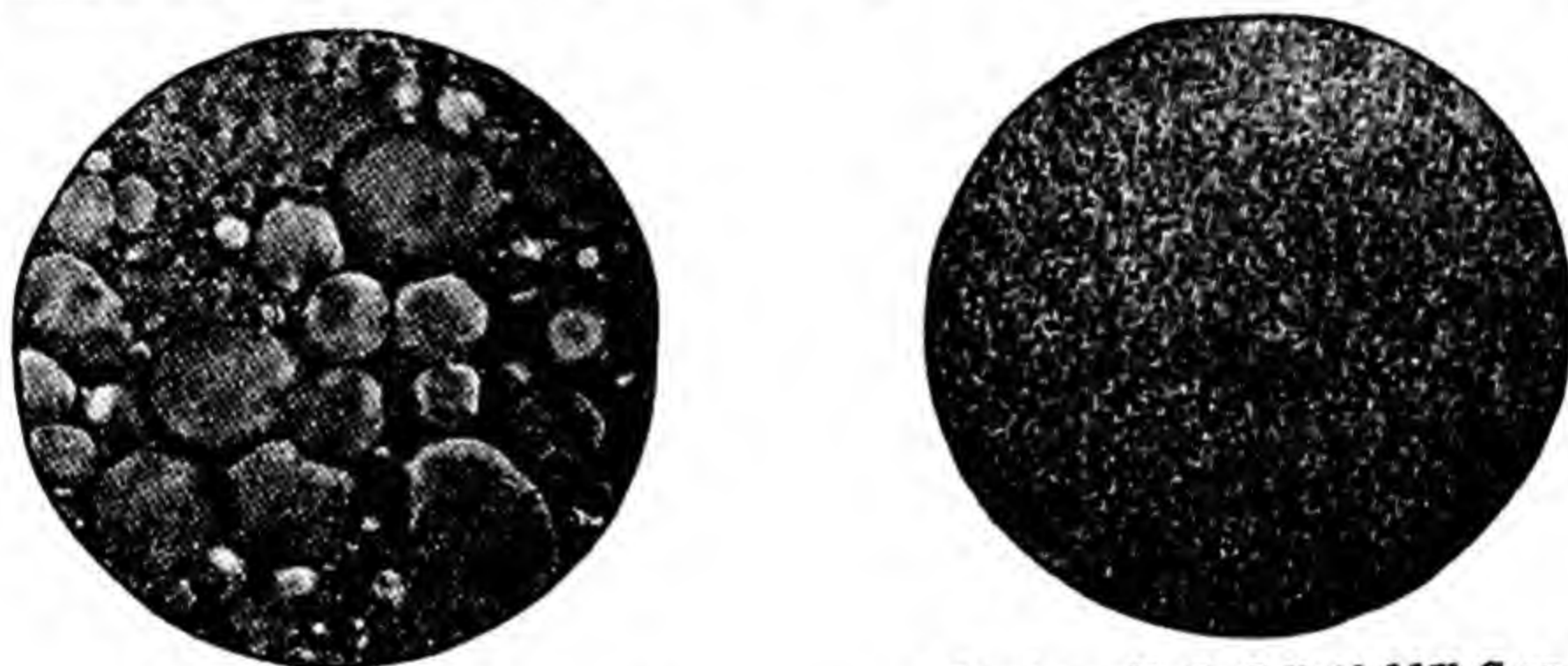
Charcoal, which is porous, has a vast surface per gram. For this reason it is used to adsorb odorous gases. The gas mask owes its efficiency in part to the presence of charcoal in the absorption chamber. Boneblack, a form of charcoal made from bones, is used in the refining of sugar and to remove yellow coloring matter from some oils. Fuller's earth is used for a similar purpose in the refining of cottonseed oil.

Emulsions. The colloidal suspensions which we have considered so far have been those of solids in liquids. Emulsions, or colloidal suspensions of liquids in liquids, have most of the properties which we have already discussed in connection with suspensions of solids. The droplets of fat in untreated milk display Brownian movement, but eventually they rise to the surface as cream. In homogenized milk the fat globules are so small that the milk and cream do not separate into two layers. It is necessary to add an emulsifying agent to some mixtures to prevent separation into layers. An egg serves as an emulsifying agent in mayonnaise dressing.

Some applications of colloid chemistry. The making of jelly depends upon the formation of a gel, which contains fruit juices.

A gel is formed when the colloidal particles of a solid take up large quantities of water and finally solidify. Pectin, a substance which is present in unripe fruit, especially apples, has this tendency to form gels. Gelatin and agar-agar also swell when placed in cold water and form typical gels. Gelatin gels containing as much as 95 per cent water are easily made. They may be cut or broken like a solid. The structure of a gel may be thought of as similar to that of a sponge, in which a netlike structure holds the liquid.

Smoke and dust are a great menace in some communities. Since these represent a typical colloidal suspension of solids in a gas, and since the particles are negatively charged, they may be precipitated by neutralizing the charge. The Cottrell precipitator



Courtesy, U. S. Colloid Mill Corp.

Fig. 125. Colloid particles. Mayonnaise dressing before (left) and after (right) passing through a colloid mill.

accomplishes this. Particles of solid which would otherwise emerge into the air from the smoke stacks of factories or smelters are made to come into contact with plates that are positively charged, and the particles settle on these plates.

The use of finely divided metals as catalysts depends on the adsorption capacity of colloids. When finely divided platinum or nickel is used in the hydrogenation of oils, it is thought that the hydrogen molecules become adsorbed on the surface of the metal to such an extent that they increase the concentration of the gas tremendously at these points. This increases the speed of the reaction between hydrogen and the oil in contact with it.

Rubber, in its natural state, is a colloidal suspension, and its preparation for use depends upon principles of colloidal chemistry. The manufacture of leather from hides is a colloidal process. Glues and adhesives are colloids. The preparation of soils for agricultural purposes, the manufacture of photographic plates and films, the silvering of glass for mirrors, certain methods of dyeing, the flotation process used in metallurgy, the manufacture of

explosives, all of these involve a knowledge of the properties of colloids.

Questions and Exercises

1. Give examples of a colloidal suspension of (a) a solid in a gas; (b) a solid in a liquid; (c) a solid in a solid; (d) a liquid in a liquid; (e) a liquid in a gas; (f) a liquid in a solid; (g) a gas in a liquid.
2. What is an emulsion?
3. How is jelly made?
4. What is the structure of a gel?
5. Explain the formation of curds in the souring of milk.
6. How is a delta formed in the mouth of a river?
7. If a river flowed into a fresh-water lake, would there be the same tendency to form a delta at its mouth?
8. Why do colloidal particles remain suspended indefinitely?
9. What is the approximate size of a colloidal particle?
10. Give one reason for believing that the molecules of a liquid are in rapid motion.

UNIT VIII

Group V of the Periodic Table: Nitrogen, Phosphorus, Arsenic, Antimony, and Bismuth

PART 1

Nitrogen

The elements of Group V—nitrogen, phosphorus, arsenic, antimony, and bismuth—have a maximum valence of 5, since they have five electrons in the outermost shell. Nitrogen and phosphorus are nonmetallic, while arsenic, antimony, and bismuth are increasingly metallic in character.

Since nitrogen is one of the most important of the elements, we shall consider its properties and its compounds in some detail.

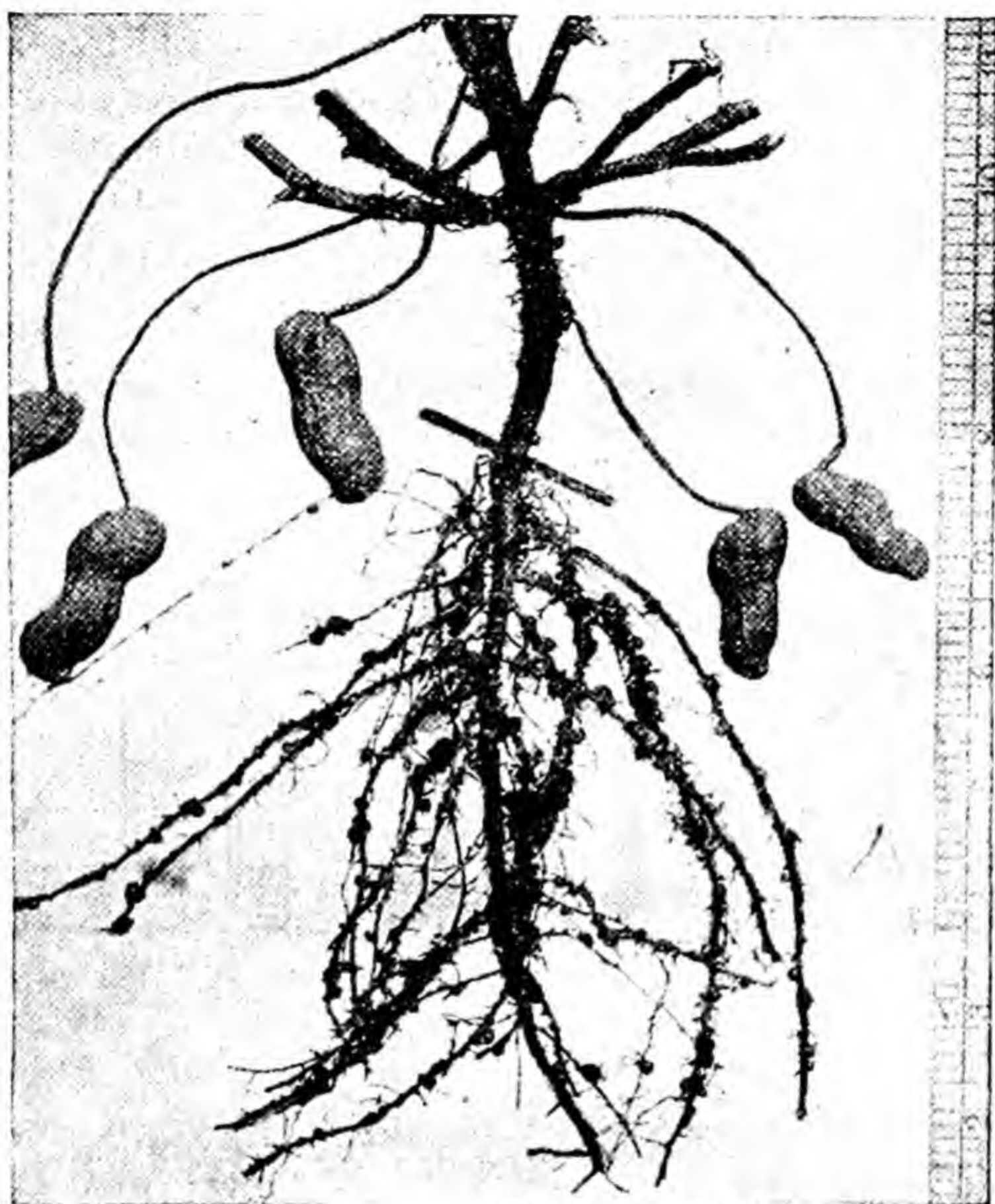
PHYSICAL PROPERTIES OF NITROGEN

Atomic weight.....	14.008
Atomic number.....	7
Isotopes.....	14, 15
Electrons in shells:	
1st.....	2
2nd.....	5
Melting point, °C.....	-210.0
Boiling point, °C.....	-195.8
Density of liquid, grams per cubic centimeter.....	0.808
Heat of vaporization, calories per mole.....	1350
Weight of liter, grams 0°, 1 atmosphere.....	1.2506

Occurrence. Nitrogen, the first member of Group V of the Periodic Table, is one of the most interesting of the chemical elements. It is often called an inert gas because it does not burn or support combustion and, although it is taken into the lungs with every breath, it is unchanged in the body, and is given back to the air when we exhale. It is, however, a constituent of every living cell in animals as well as in plants.

Nitrogen is really not an inert element; it forms many compounds. Among these are salts called *nitrates*, which exist in the soil. Plants absorb these nitrates from the soil through their roots and utilize the nitrogen obtained in this way in making nitrogen compounds called *proteins*. Proteins constitute a neces-

sary part of our diet, and we obtain these essential compounds from the fruits and vegetables we eat and from meat, eggs, and milk. The nitrogen compounds in meats, eggs, and milk are derived from plant life also, for plants constitute the ultimate source of food for all animals.



Courtesy, U. S. Dept. of Agriculture

Fig. 126. Nodules on the roots of a peanut plant.

Nitrogen fixation by bacteria. Although there is an abundant supply of *free nitrogen* in the air, we have only a limited quantity of *fixed nitrogen*; that is, nitrogen chemically combined with other elements. Many basic industries, including agriculture and mining, are dependent upon nitrogen compounds. Our national defense is based upon the use of nitrogen compounds. Maintenance of life upon the earth depends not upon free nitrogen but upon nitrogen compounds. To meet these requirements chemists in every civilized country have tried to find ways to convert atmospheric nitrogen into nitrogen compounds such as nitric acid or ammonia. Until the beginning of the twentieth century we were entirely dependent upon the activities of bacteria in the soil for this accomplishment, but nitrogen compounds are now

made in many laboratories. The chemical methods that have been developed to convert free nitrogen of the air into compounds will be described later.

The decay of dead vegetable and animal matter is brought about by bacterial action. Some of the nitrogen in such organic matter is released as free nitrogen gas, and some of it is converted into ammonia. Certain bacteria are able to oxidize ammonia to nitrites (salts of nitrous acid), and other micro-organisms convert nitrites into nitrates (salts of nitric acid). In nitrates the nitrogen is once more in a form that plants can use. Only part of the nitrogen used by any crop gets back into the soil in this way. The rest of it goes into the air as free nitrogen.

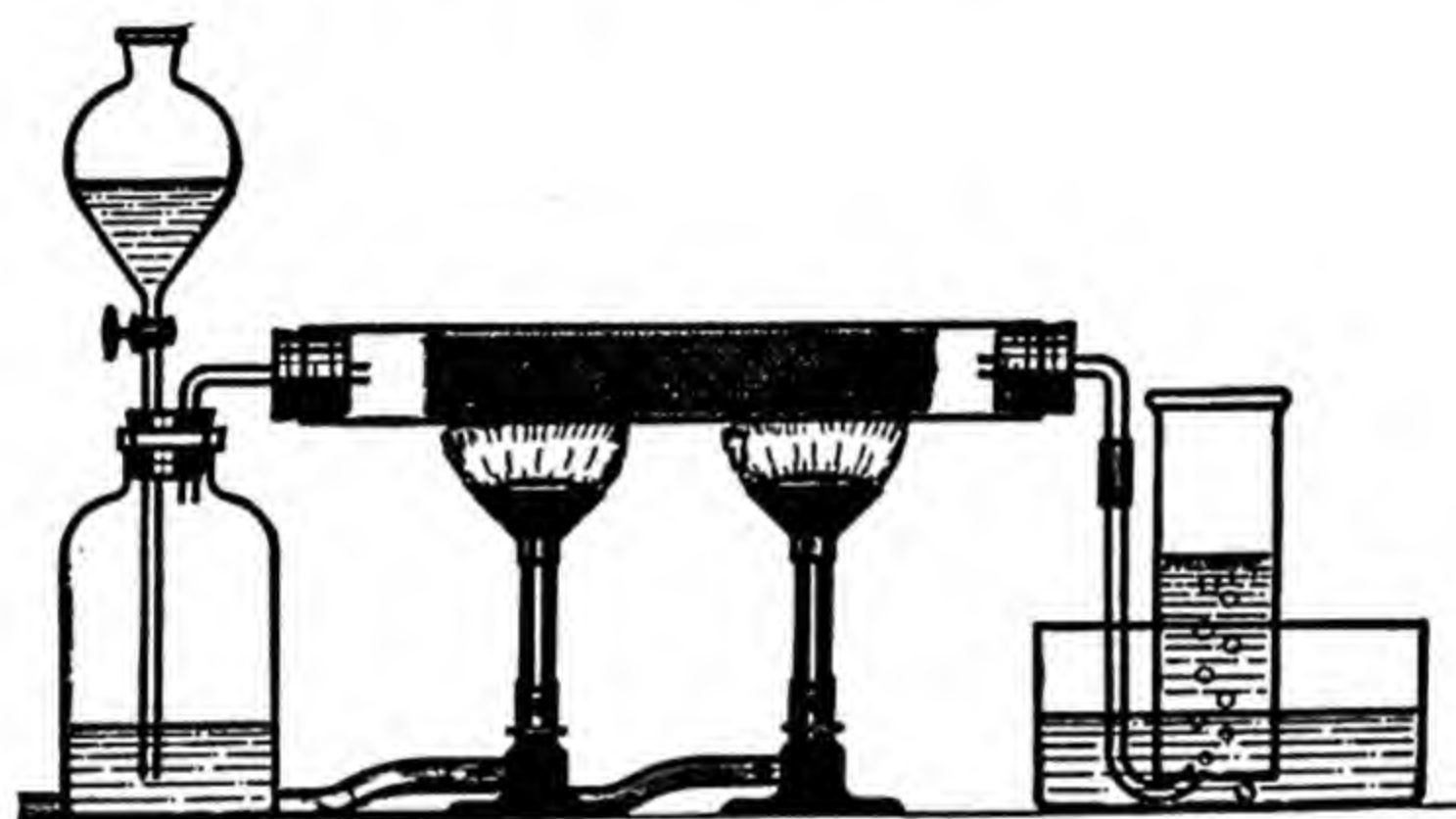
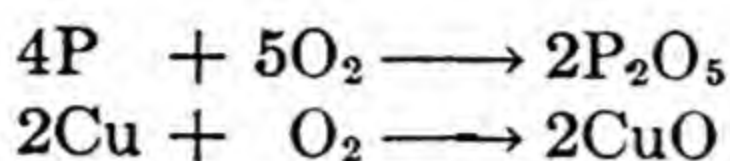


Fig. 127. Preparation of nitrogen from the air. The air is forced over hot copper gauze.

There are a few species of bacteria that are able to utilize atmospheric nitrogen and convert the gas into water-soluble nitrogen compounds in the soil. These are found on the roots of certain leguminous plants, including lupins, clover, alfalfa, and peas. Clumps of these bacteria form small nodules on the roots of these plants. When the nitrogen compounds have been removed from the soil, it is customary to plant the field with clover or alfalfa for a season or two, for these crops are not dependent upon the presence of nitrogen compounds in the soil. Then the green crop of clover or alfalfa is plowed under, and as the vegetable matter decays, a fresh supply of combined nitrogen is left in the soil.

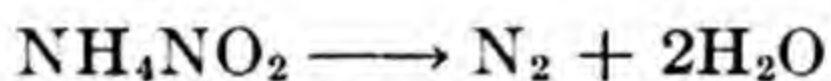
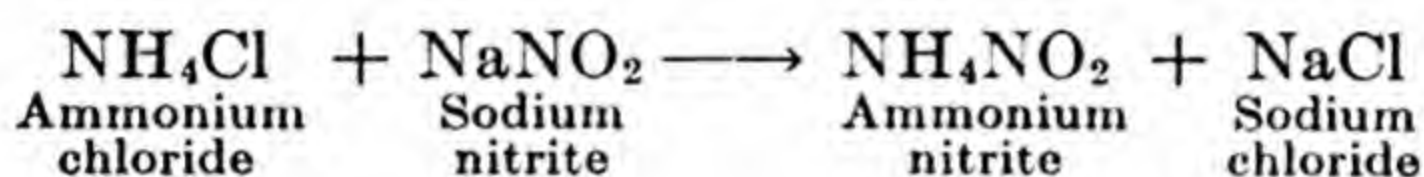
Preparation of nitrogen. Since the air is 80 per cent nitrogen, it would seem logical to prepare the element from the air. However, there are always some impurities in the gas when it is made this way. For practical purposes, where a small amount of impurity does not interfere with its use, nitrogen is often made by removing the oxygen from the air with phosphorus or hot

copper. The reactions involved are represented by the following equations:

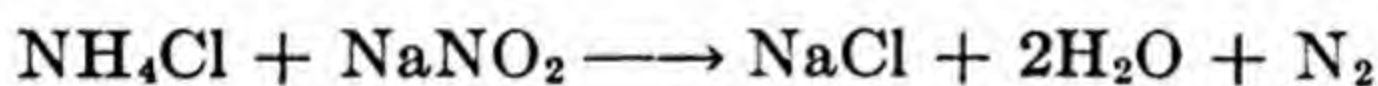


A large amount of nitrogen is produced commercially from liquid air. Since liquid nitrogen has a lower boiling point than liquid oxygen, it becomes warm enough to boil and change to a gas before oxygen does. It is stored and transported in cylinders, under pressure. It always contains a small amount of oxygen when prepared in this way.

Laboratory preparation. Pure nitrogen is obtained by heating a mixture of ammonium chloride and sodium nitrite. Ammonium nitrite, a very unstable salt, is formed in this process, but it decomposes at once into water and nitrogen.



The result of the two reactions shown above may be represented by one equation as follows:



Physical properties of nitrogen. Nitrogen is a colorless, tasteless, and odorless gas. It is slightly soluble in water—less soluble than oxygen. Nitrogen forms a colorless liquid when compressed and then cooled to a very low temperature. On further cooling it changes to a white solid. Nitrogen gas has the formula N_2 ; its molecular weight is 28.

Chemical properties of nitrogen. Nitrogen does not support combustion. If a burning splinter is inserted in a bottle of nitrogen, the flame is extinguished. Nitrogen in the air slows down the burning of substances. We saw how much faster many substances burn in pure oxygen than in air. Nitrogen dilutes the oxygen, thus preventing it from making rapid contact with the burning substance. The nitrogen also gets hot, which means that it removes heat from the burning substance and from the oxygen surrounding it. This removal of heat also retards the rate of burning.

Under certain conditions nitrogen combines with hydrogen to form ammonia, and, at the temperature of the electric arc, nitrogen combines with oxygen, forming oxides of nitrogen. Reactions between nitrogen and oxygen take place in the air during

a thunderstorm. When lightning passes through the air, a small amount of nitric oxide, NO , is formed.

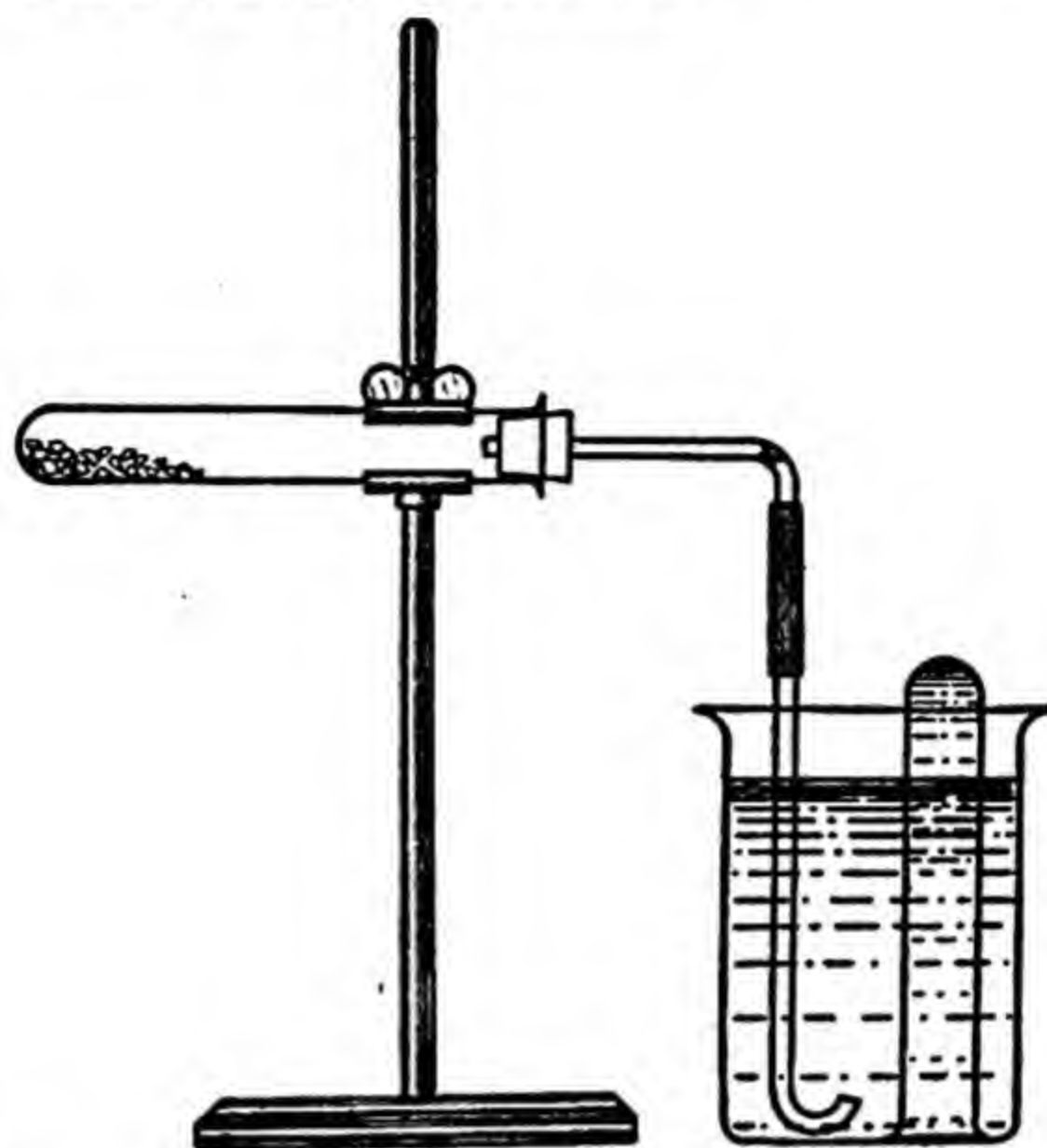


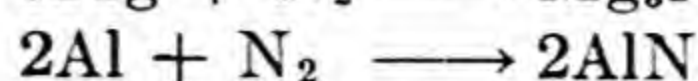
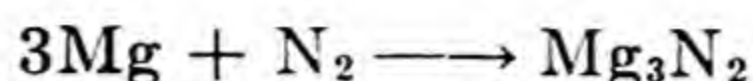
Fig. 128. Preparation of nitrogen from an ammonium salt and a nitrite.

The compounds of nitrogen are easily decomposed. Most of our common explosives, such as gunpowder, nitroglycerine, gun-cotton, T.N.T., and blasting gelatin, contain nitrogen.



Fig. 129. One of Nature's ways of making nitric acid.

Nitrogen combines directly with very hot aluminum, calcium, and magnesium to form nitrides:



Questions and Exercises

1. What per cent of the atmosphere is nitrogen gas?
2. Outline a method for obtaining nitrogen from the air.
3. Describe a method for obtaining nitrogen from a compound.
4. In what form is nitrogen used by plants?
5. What is meant by the term "fixed nitrogen"?
6. In the preparation of a radio vacuum tube, a small amount of magnesium is placed in the tube, and after almost all the air has been pumped out, the tube is sealed. Finally the small amount of air remaining in the tube is removed by reaction with magnesium vapor, which is formed by heating the closed tube. What reactions occur which "clean up" the nitrogen and oxygen?
7. From the formula, N_2 , determine the weight of 1 liter of nitrogen under standard conditions of temperature and pressure.
8. (a) How many grams of nitrogen can be prepared by heating 107 g. of ammonium chloride with NaNO_2 ? (b) How many grams of sodium nitrite will be required?
9. How many liters of nitrogen, measured under standard conditions, can be prepared by heating 192 g. of ammonium nitrite?
10. How many liters of nitrogen can be prepared by removing the oxygen from 100 liters of air?
11. Why does a splinter burn more slowly in air than in pure oxygen?
12. Why do farmers "rotate" crops?
13. Calculate the percentage of nitrogen in ammonium nitrite.
14. When air dissolves in water, the proportion of nitrogen to oxygen which dissolves in the water is not the same as in the air. How does this prove that air is a mixture of gases and not a compound?

PART 2

Ammonia

Occurrence. Ammonia is a colorless gas with a pungent odor. Small amounts of it are found in the air, in natural waters, and in the soil. When animal or vegetable matter decomposes, much of the nitrogen in the proteins of the decaying substance is converted into ammonia. The characteristic odor of ammonia can usually

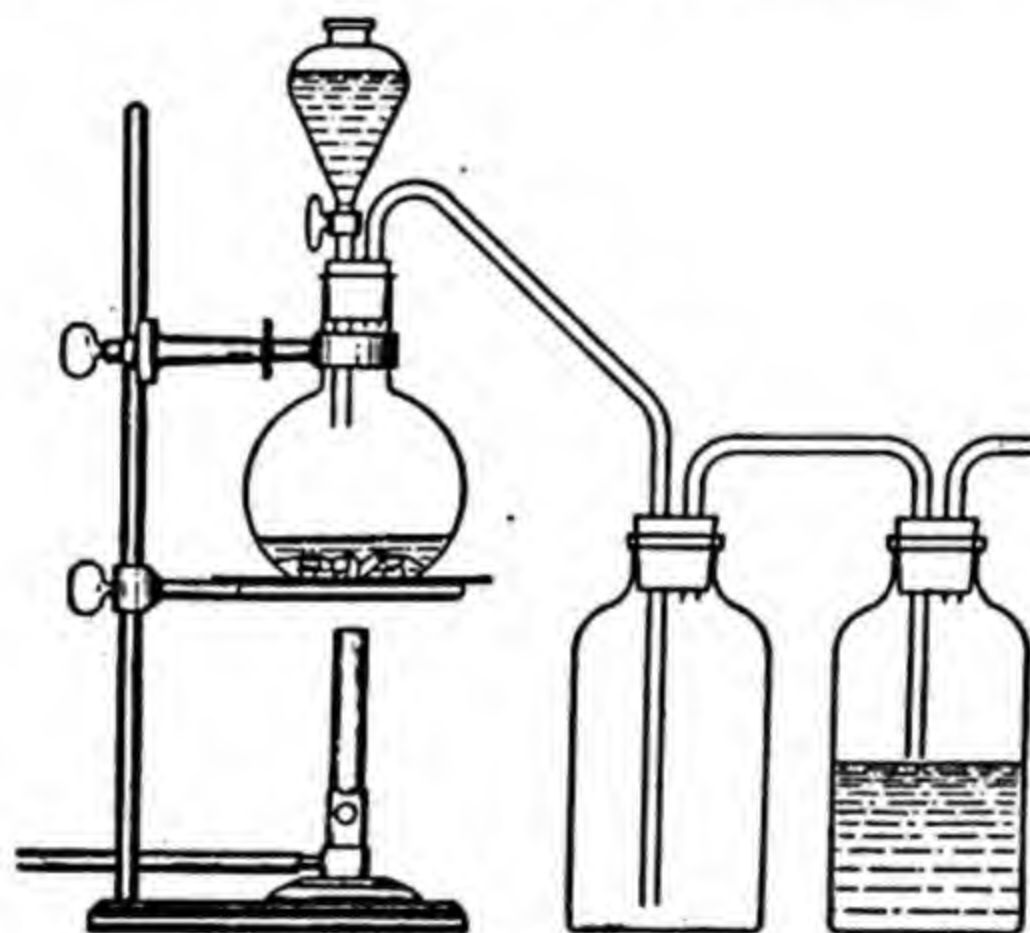
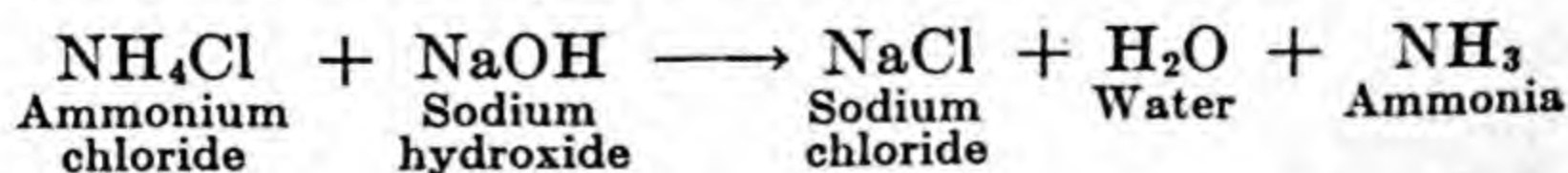


Fig. 130. Laboratory preparation of ammonia.

be noticed in the neighborhood of a decomposing substance of this type.

Laboratory preparation. Ammonia is prepared in the laboratory by heating any ammonium salt, such as ammonium chloride, with a solution of a base, sodium hydroxide for example:



Usually calcium hydroxide, $\text{Ca}(\text{OH})_2$, is used rather than the more expensive sodium hydroxide.

Physical properties. Ammonia gas is only about half as dense as air, and it is collected by allowing it to flow upward into an inverted bottle. At 20°C ., one volume of water dissolves about 700 volumes of ammonia, and at 0°C . the solubility is much greater

(1200 to 1). The aqueous solution is ordinary ammonia water or ammonium hydroxide. Commercial concentrated ammonium hydroxide is approximately 35 per cent NH_3 by weight.

The great solubility of ammonia may be shown by a fountain experiment similar to the one described on page 194.

Ammonia condenses to a liquid at 0°C . if the pressure on the gas is equal to at least 4.2 atmospheres. This liquid, true liquid ammonia, must not be confused with a solution of ammonia gas in water.

Chemical properties. The most important chemical property of ammonia is its capacity to combine with water to form ammonium hydroxide. This base is formed when the gas is dissolved in water. Only a part of the dissolved gas, however, reacts with water, forming NH_4OH molecules. The rest of it is in the form of NH_3 molecules. Ammonium hydroxide is a weak base; that is, only a small percentage of its molecules are dissociated into ions. Most of the ammonium hydroxide, formed by a combination of NH_3 and water, is in the form of molecules. The behavior of ammonia in water is represented by the equation:



The arrows pointing in both directions show that the different substances appearing in the equations are in *equilibrium* with each other. This condition means that all these substances—ammonia, ammonium hydroxide, ammonium ions, hydroxide ions, and water—are present in the solution. If we remove a portion of any one of these components of the solution, more of the substance removed is formed immediately from the other ions and molecules present. If, for example, NH_3 is removed from the solution by leaving the container open to the air, or by warming it, we shall find that ultimately only pure water remains in the container. As the ammonia gas is removed from the solution, the reactions tend to go from right to left:

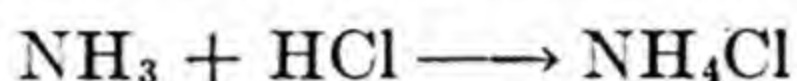


Some of the ammonium hydroxide decomposes into NH_3 and water, trying to replace the NH_3 that has been removed. At the same time, ammonium and hydroxide ions combine to form molecular ammonium hydroxide, in an attempt to maintain some of this substance in the solution. If ammonia is continuously removed, nothing but water remains at the end of the experiment.

If hydroxide ions are removed by neutralization with an acid, the reactions tend to go toward the right. More NH_4OH dissociates into ions, attempting to keep the OH^- concentration

constant. At the same time more ammonia gas combines with water to form NH_4OH molecules to keep up the supply of this component. If hydrogen ions are gradually added to the solution, removing hydroxide ions as fast as they are formed, finally all the ammonia and undissociated ammonium hydroxide molecules will be entirely removed. The solution will contain only ammonium ions and the negative ion of the acid. On evaporation these combine to form the ammonium salt of the acid.

Clouds of ammonium chloride are formed whenever open bottles of ammonium hydroxide and hydrochloric acid are brought near each other, for the escaping gases react as follows:



Reagent bottles filled with hydrochloric acid and ammonium hydroxide often become coated with a thin covering of ammonium chloride as they stand on the shelves.

Commercial preparation of ammonia. Ammonia was formerly made by heating hoofs, horns, and other organic materials containing nitrogen compounds. A solution of the gas was called "spirits of hartshorn." At the present time ammonia is made by one of the following methods:

1. *From soft coal.* When soft coal is heated, as in the manufacture of coke, ammonia is one of the gases which escape. The nitrogen compounds of carbon in the coal are decomposed by heat, liberating ammonia. This is separated from the other gases by passing the mixed gases through water. The ammonia dissolves in the water and is then neutralized with sulfuric acid, forming ammonium sulfate. On evaporation of the water, solid ammonium sulfate is obtained. Ammonia is recovered from this salt by treatment with lime.

2. *The Haber process.* One of the most important chemical developments of recent years has been the production of ammonia by the direct combination of hydrogen and nitrogen gases.



A German chemist, Fritz Haber, was the first to successfully accomplish this direct union between the gases. When nitrogen and hydrogen are mixed at ordinary temperatures, practically no reaction takes place between the two gases. If the mixture is heated, a small amount of ammonia is formed, but heat is given out during the reaction, and the consequent rise in temperature decomposes some of the ammonia into its elements. A state of equilibrium is soon reached, in which the yield of ammonia is very small.

It is evident that a catalyst must be used to make the reaction take place at a reasonable rate at a temperature low enough to avoid decomposition of the ammonia. As a catalyst, Haber employed iron oxide mixed with molybdenum, uranium, or cobalt. Many other satisfactory catalysts have been found, probably the most successful being one developed by the Fixed Nitrogen Laboratory in Washington. It consists of porous iron mixed with a small amount of potassium aluminate. Even with the use of an efficient catalyst, the yield of ammonia is so small that the process is not commercially practical unless the reaction mixture is kept under high pressure. When nitrogen and hydrogen combine to form ammonia, 1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia; there is a decrease in the total volume of gases. It is a general law, first stated by Le Chatelier, that an increase in pressure always tends to produce the system having the smaller volume, the decrease in volume tending to relieve the effect of the applied pressure.

Whenever pressure is exerted on anything in nature, the substance tries to escape from that pressure, if possible. If a heavy weight is placed on a block of ice, the ice melts. Liquid water has a smaller volume than ice. Ice therefore changes into its liquid form in an effort to escape the increased pressure.

In the Haber process, hydrogen and nitrogen can reduce the pressure placed upon them by combining and forming a gas with a smaller volume. Hence the use of pressure tends to increase the production of ammonia. Pressure is applied in all processes involving gas reactions if the desired product has a smaller volume than that of the gases from which it is made. We shall find more applications of this principle later.

The effect of both temperature and pressure on the yield of ammonia is shown in the following table:

YIELD OF NH_3 IN PER CENT BY VOLUME

Temperature, °C.	Pressure in atmospheres			
	30	100	300	600
200	67.6	81.5	90.0	95.4
300	30.3	52.0	71.0	84.2
400	10.2	25.1	47.0	65.2
500	3.5	10.6	26.4	42.1
600	1.4	4.2	13.8	23.1
700	0.7	2.2	7.3	12.6

Although the yield of ammonia is greater at lower temperatures, the speed of the reaction is so slow that it is not practical to use these temperatures. Recently developed plants operate at temperatures of 500° to $600^{\circ}\text{C}.$, and at pressures of 100 to 200 atmospheres. The French Claude process works at pressures of 600 to 1000 atmospheres. At these great pressures iron is permeable to hydrogen, and the containers must be constructed of chrome-steel alloys.

As the nitrogen and hydrogen pass over the catalyst, some ammonia is formed. The mixture of gases is then passed through a cooling coil, where the NH_3 is condensed to a liquid and removed. The unchanged N_2 and H_2 , together with an additional charge, are returned to the hot catalyst.

3. *The cyanamide process.* When nitrogen gas is passed over white-hot calcium carbide, calcium cyanamide and carbon are formed:



The cyanamide is then hydrolyzed by treatment with superheated steam:



Uses of ammonia. Large quantities of ammonia are used in making soda by the Solvay process. Ammonia is used also in the production of nitric acid, and in the cooling units of modern refrigerators.

Ammonia is easily liquefied by compression. When the pressure is removed, the liquid ammonia boils, passing rapidly into the gaseous state. In doing this it absorbs heat from its surroundings, leaving everything in its vicinity colder.

This cooling is the principle used in the mechanical refrigerator. Ammonia gas is first compressed by a pump. When a gas is compressed, it becomes hot. The heat is removed by allowing water to trickle over the pipes containing the compressed gas or by blowing air over the pipes. As soon as it is cooled, the ammonia liquefies and the liquid is conveyed to the region which is to be cooled. The pressure is then removed, and the liquid vaporizes, absorbing heat during the process (see Heat of Vaporization, Unit II, Part 4). This heat absorption cools the air or water surrounding the pipes in which the expansion occurs.

Ammonia, sulfur dioxide, and freon are the gases commonly used in refrigeration, because they can be liquefied at ordinary temperatures with moderate compression. Freon is the trade

name for dichlorodifluoromethane, CCl_2F_2 . It is a gas which is easily liquefied, and the liquid boils at -30°C .

The heat of vaporization of liquid ammonia is 330 cal. per gram. Every gram of liquid ammonia in passing into the gaseous state must absorb 330 cal. of heat from its surroundings. The removal of this quantity of heat from water which has been cooled to 0°C . produces more than 4 g. of ice. (The heat of fusion of ice is 79 cal. per gram. See page 72.)

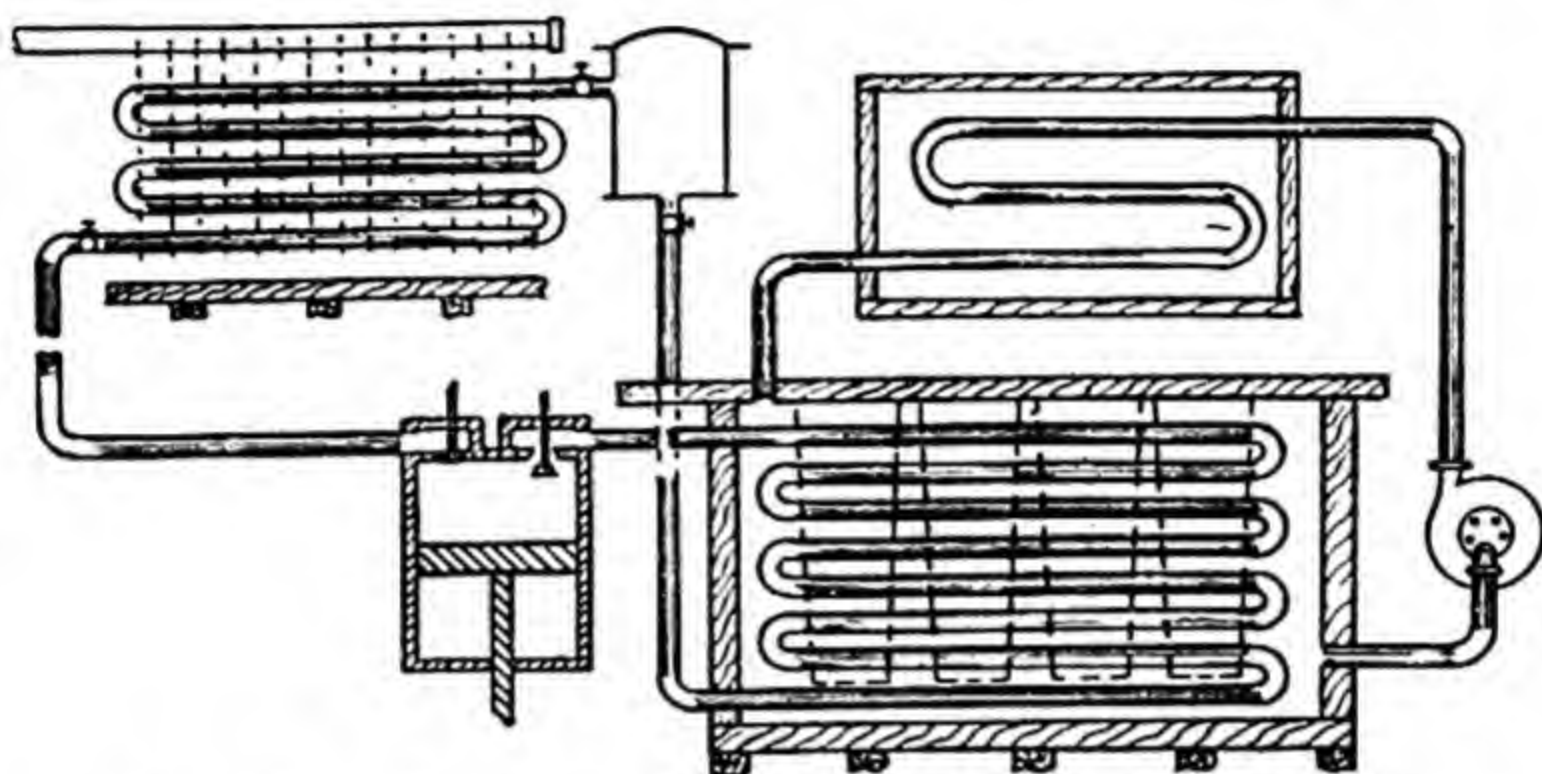


Fig. 131. Diagram of an artificial ice plant. Gas is compressed by the pump and forced into the upper left-hand coils. Water trickling over these coils cools and liquefies the ammonia. The liquid is allowed to vaporize and expand in the lower right-hand coils. These coils are submerged in brine. The heat absorbed by the ammonia, in vaporizing, lowers the temperature of the brine below the freezing point of water. Artificial ice is made by placing tanks containing pure water in this cold brine.

Ammonium salts. The most important ammonium salts are the chloride and the sulfate. Ammonium chloride, often called "sal ammoniac," is used in dry cells and in most soldering pastes. Ammonium sulfate, a white powder, is used extensively as a fertilizer.

Questions and Exercises

1. Give two uses for ammonia.
2. How could you distinguish between nitrogen and ammonia?
3. Calculate the percentage composition of ammonia.
4. Slaked lime and ammonium sulfate, when mixed and warmed, react as follows:



What volume of ammonia measured under standard conditions can be liberated from ammonium sulfate by 28 g. of slaked lime?

5. Explain why the Haber process is carried out under very high pressures.

6. If pure hydrogen can be produced for 5 cents per pound and pure nitrogen for 1 cent per pound, what is the cost of the raw materials necessary to make 100 lb. of ammonia?

7. Ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$, also known as smelling salts, decomposes slowly at room temperature to yield ammonia as one of the products. Write an equation representing the decomposition.

8. How is ammonia gas obtained from ammonium chloride?

9. Is ammonia soluble in water?

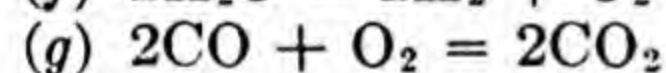
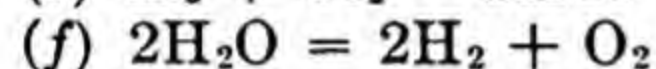
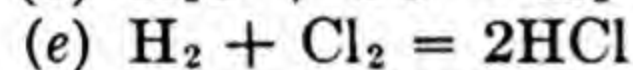
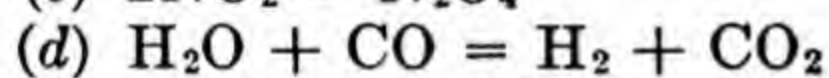
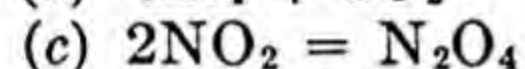
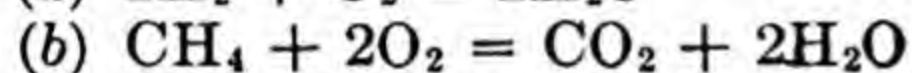
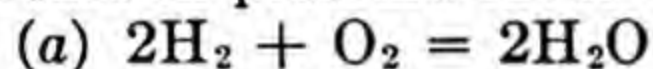
10. How would you test an unknown sample for the presence of an ammonium salt?

11. In the preparation of ammonia gas, why is the gas collected by displacement of air and not by displacement of water?

12. Is an aqueous solution of ammonia neutral, basic, or acidic?

13. Nitrogen may be prepared by passing ammonia gas over heated copper oxide, the copper oxide taking part in the reaction. Write the equation for the reaction and make a sketch of an apparatus suitable for this preparation.

14. In which of the following equations for reactions between gases will an increase in pressure favor the formation of the products indicated:



15. What substances are present in the solution when ammonia gas is dissolved in water?

16. If a bottle of ammonium hydroxide is left open to the air, why does it lose all odor of ammonia?

17. Write the equation for the reaction that takes place when ammonia is passed into a solution of (a) hydrochloric acid; (b) sulfuric acid; (c) carbonic acid.

18. Name two ways in which ammonia is made for commercial use.

19. Distinguish between the words *ammonia* and *ammonium*.

20. (a) How many liters of ammonia are formed when 10 liters of nitrogen combine with hydrogen to form ammonia? (b) How many liters of hydrogen are used?

21. The formula for ammonia is NH_3 . What is the weight of 1 liter of the gas?

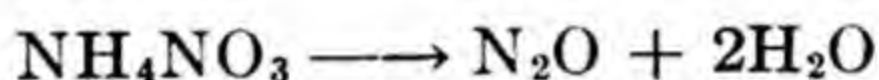
PART 3

Oxides and Acids of Nitrogen

Nitrogen forms five oxides. These are *nitrous oxide*, N_2O ; *nitric oxide*, NO ; nitrogen dioxide, NO_2 ; nitrogen trioxide, N_2O_3 ; and nitrogen pentoxide, N_2O_5 .

Nitrogen combines with hydrogen and oxygen to form a series of acids. The most important members of the group are *nitrous acid*, HNO_2 , and *nitric acid*, HNO_3 .

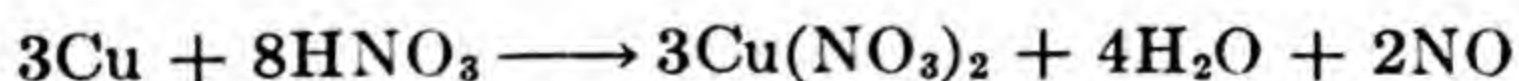
Nitrous oxide (N_2O). This gas is prepared readily by heating ammonium nitrate:



Nitrous oxide is often called "laughing gas." When inhaled in small amounts, it may cause a sort of hysteria. Larger amounts of the gas cause insensibility to pain and unconsciousness. Mixed with oxygen, it is used as an anesthetic for minor operations, including dentistry.

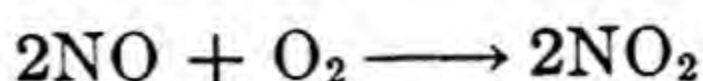
Nitrous oxide is a colorless gas with a slightly sweet odor. It supports combustion almost as readily as oxygen does. A glowing splinter ignites and burns as brightly in nitrous oxide as it does in oxygen. Carbon, iron, and phosphorus also burn readily in nitrous oxide, forming the same compounds that they form when burned in oxygen. Nitrogen gas is liberated from the nitrous oxide in these reactions. This activity shows that the nitrogen and oxygen atoms must be held together very loosely in the molecule of the compound.

Nitric oxide (NO). Nitric oxide is made in the laboratory by the action of dilute nitric acid on copper:



It is a colorless gas which can be collected by the displacement of water, for it is only slightly soluble in water. When a bottle of nitric oxide is opened to the air, a dark brown gas forms in the mouth of the bottle. The brown gas is nitrogen dioxide. It is

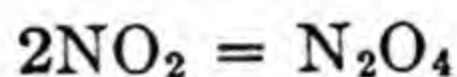
formed by a reaction between nitric oxide and the oxygen of the air:



Nitric oxide supports the combustion of some substances which are already burning briskly and giving out large amounts of heat. Magnesium and phosphorus burn readily in nitric oxide.

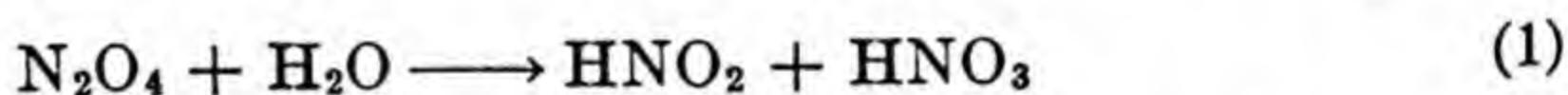
Nitric oxide is formed in small amounts in the air during a thunderstorm. A flash of lightning causes some of the nitrogen and oxygen in its path to combine to form this gas.

Nitrogen dioxide (NO_2). This brown gas, formed by the combination of oxygen and nitric oxide, is very irritating to the mucous membrane. When cooled, the gas becomes light in color, owing to the formation of light-colored molecules having twice the molecular weight of the brown gas:

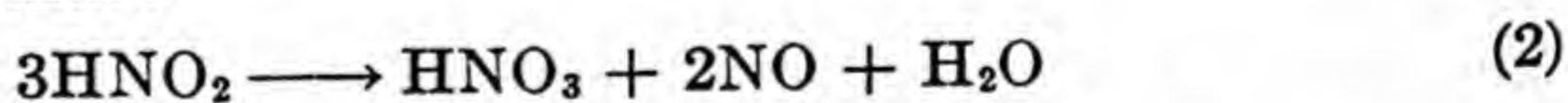


At 22°C ., about 75 per cent of the gas is in the form of the tetroxide, N_2O_4 . As the gas is heated, the *nitrogen tetroxide* molecules decompose again, forming the brown gas nitrogen dioxide.

Nitrogen tetroxide is very soluble in water. In cold water the first products formed are nitrous acid, HNO_2 , and nitric acid, HNO_3 :



Nitrous acid does not, however, increase in the solution beyond a certain concentration, for it decomposes readily, forming nitric acid and nitric oxide:



The nitric oxide released in this process reacts with oxygen of the air, forming more nitrogen tetroxide, and is returned to water to react as in equation (1).

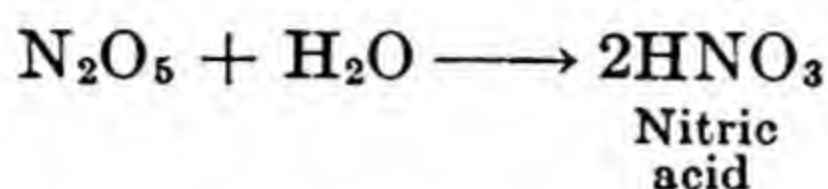
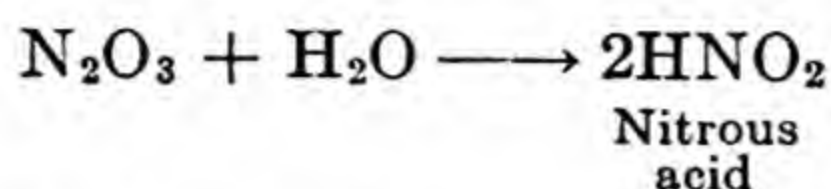
When the gas is passed into warm water, the main reaction may be written as follows:



Two-thirds of the NO_2 (or N_2O_4) is converted into nitric acid, and the NO which escapes is not wasted. It is allowed to react with air to form NO_2 , and the process is repeated. Each time, two-thirds of the nitrogen used is converted into nitric acid.

Other oxides. *Nitrogen trioxide*, N_2O_3 , is a brown gas, and *nitrogen pentoxide*, N_2O_5 , is a white solid. They are both unstable and unimportant compounds, and methods of making them will

not be described here. They are the anhydrides of nitrous acid and nitric acid, respectively.



Nitrous acid (HNO_2). Nitrous acid at low temperatures is a blue liquid. It decomposes readily, when warmed, into oxides of nitrogen and water. Its sodium salt, sodium nitrite, NaNO_2 , finds extensive use in the manufacture of dyes. The free acid is usually prepared by treating sodium nitrite with dilute sulfuric acid:



Nitric acid. Nitric acid and the nitrates are the most important compounds of nitrogen. The nitrates are the only compounds of nitrogen that are found in nature in large amounts. Great deposits of sodium nitrate occur in Chile, and the compound is often called "Chile saltpeter" to distinguish it from ordinary saltpeter, which is potassium nitrate. Chile saltpeter is used in one process for making nitric acid.

Pure nitric acid is a colorless liquid. It is soluble in water, and the ordinary nitric acid used in the laboratory is a solution of nitric acid in water.

Preparation. Nitric acid is usually prepared in the laboratory by heating sodium nitrate with concentrated sulfuric acid. The following reaction takes place:



If an excess of sodium nitrate is used and the mixture is heated strongly, the reaction proceeds as follows:



Since nitric acid has a lower boiling point than sulfuric acid, it is readily distilled from the mixture. The vapor may be condensed to produce pure liquid nitric acid, or it may be dissolved in water to form the aqueous solution commonly used in the laboratory. In the laboratory the mixture of sodium nitrate and sulfuric acid is heated in a glass-stoppered retort, for cork stoppers and rubber tubing are decomposed by hot nitric acid.

Commercial preparation. Three processes for the manufacture of nitric acid on a commercial scale are now in use: (1) the process

of preparation from sodium nitrate and sulfuric acid; (2) the oxidation of ammonia; (3) from nitric oxide made by the direct combination of the elements.

1. *Preparation from sodium nitrate.* For many years the only process known for the preparation of nitric acid was that of treating Chile saltpeter with sulfuric acid. The equation for the process is the same as that for the laboratory preparation given above. The reaction is carried out in huge iron retorts.

Since, however, any natural deposit of nitrates on the earth is sure to be exhausted in time, chemists have tried many plans for making nitric acid from the inexhaustible supply of nitrogen

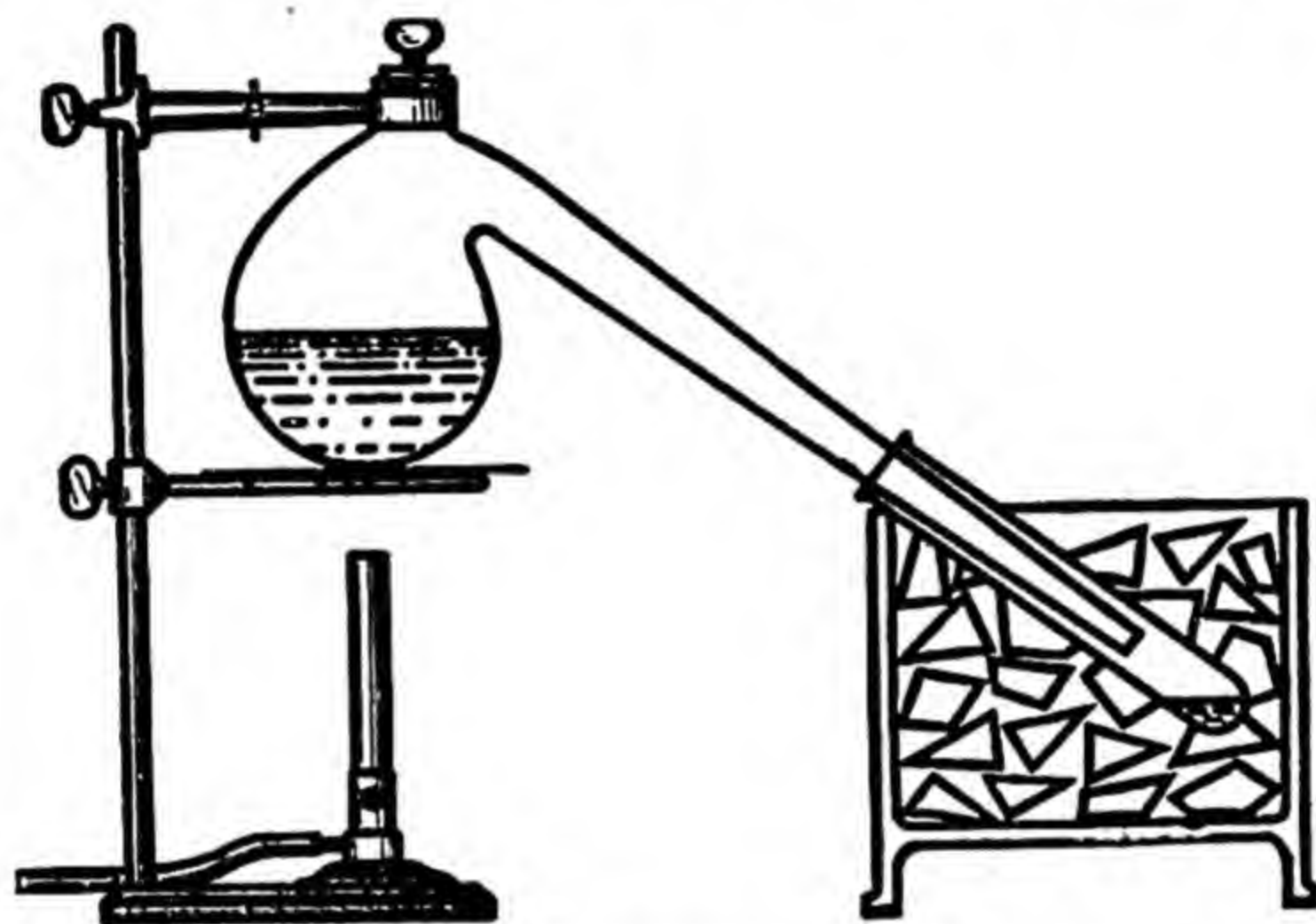
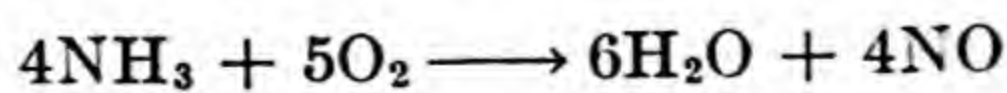


Fig. 132. Laboratory preparation of nitric acid.

in the atmosphere. Several methods for using the nitrogen of the air are now in successful operation.

2. *Oxidation of ammonia.* The most important methods depend upon the conversion of atmospheric nitrogen into ammonia and subsequent oxidation of the ammonia to nitric acid. For the methods of obtaining ammonia, see the Haber process and the cyanamide process, pages 254, 256. Ammonia is oxidized by mixing it with air and forcing the gaseous mixture through a closely woven, hot platinum gauze. The platinum catalyzes the reaction. Sufficient heat is liberated to keep the gauze at the proper temperature. In starting the process, the gauze is brought up to the right temperature by means of an electric current. The oxidation proceeds mainly according to the equation

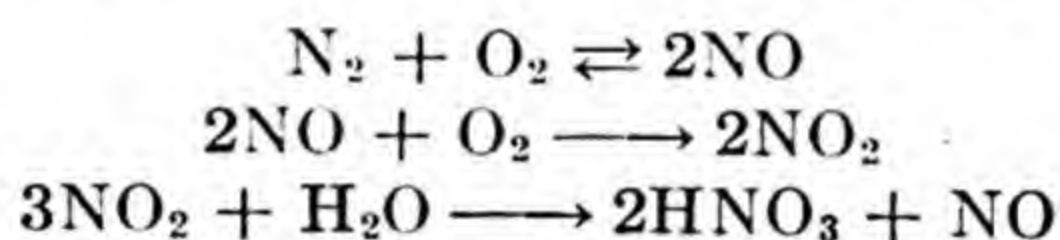


The nitric oxide combines with oxygen, forming NO_2 , which dissolves in water to form nitric acid (see page 260).

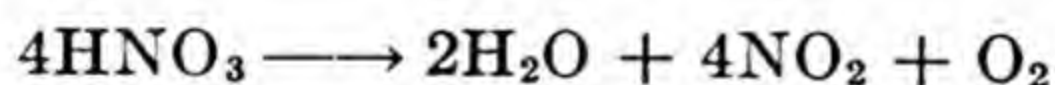
3. *The arc process.* Nitric oxide can be made from its elements only at very high temperatures. The equilibrium amounts of nitrogen and oxygen in combined form at various temperatures are indicated below.

Temperature, °C.....	1227	1727	2227	2627	2927	3927
Per cent of N ₂ and O ₂ combined.....	0.1	0.6	1.8	3.2	4.2	10.0

In order to obtain a large enough yield of nitric oxide to make the process of commercial importance, high temperatures must be employed. Actually, temperatures as high as 2000°C. are used. The mixture of nitrogen and oxygen is blown through a huge electric arc, then cooled rapidly. If the gases were cooled slowly, some of the nitric oxide would decompose, since the amount of this gas in equilibrium with nitrogen and oxygen at lower temperatures is less than at high temperatures. The cooled nitric oxide then reacts with some of the oxygen to form nitrogen dioxide, which is then dissolved in water. The equations are:

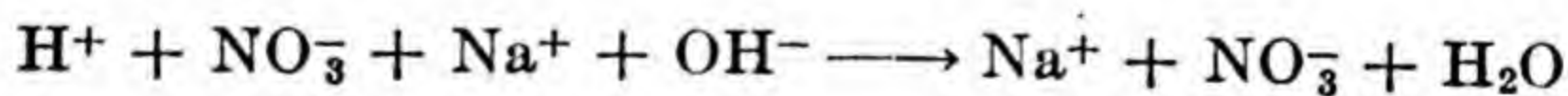


Physical and chemical properties. Pure nitric acid is colorless, but the acid made in the laboratory has a yellow color. This color is due to decomposition of part of the nitric acid at the high temperatures used:

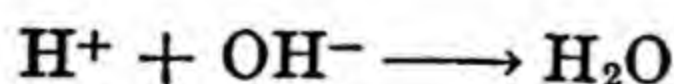


A study of the chemical properties of nitric acid is not so simple a task as the study of hydrochloric acid, because nitric acid acts not only as a strong acid, but also as an oxidizing agent.

Sodium hydroxide neutralizes nitric acid, as indicated by the following equation:

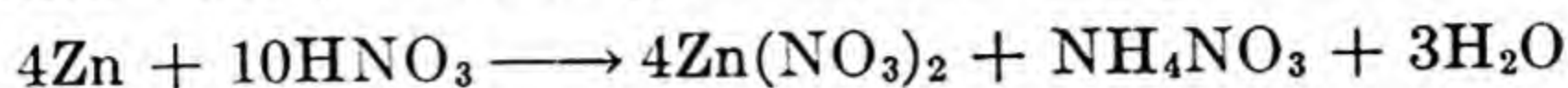


or

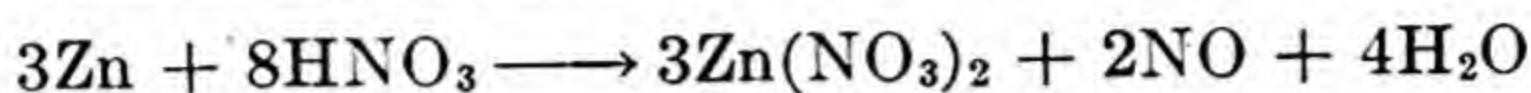


This reaction is exactly like that between sodium hydroxide and hydrochloric acid, but the action of nitric acid on a piece of zinc is not like the action of hydrochloric acid on zinc. No hydrogen is evolved when nitric acid acts upon zinc. The products formed depend upon the temperature and concentration of the acid. Cold,

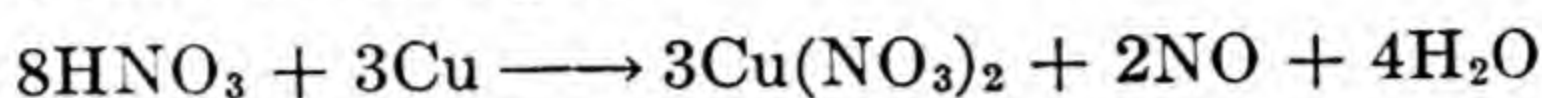
dilute nitric acid acts upon zinc to form zinc nitrate, ammonium nitrate, and water, according to the following equation:



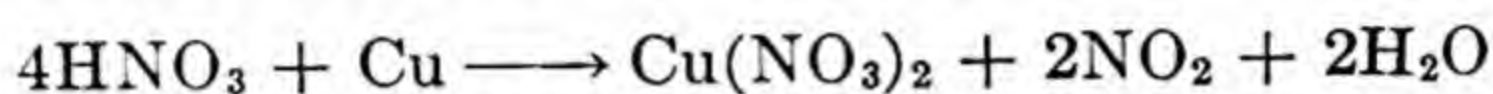
With more concentrated acid the reaction proceeds as follows:



Moderately concentrated nitric acid acts upon copper to form water and oxides of nitrogen:

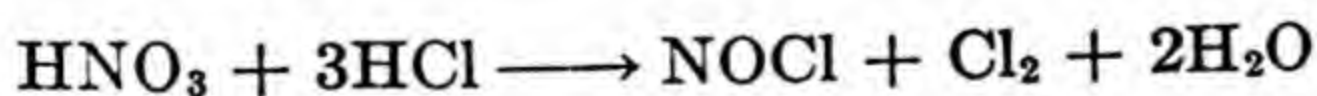


More concentrated acid liberates nitrogen dioxide:



Test. The common test for the nitrate ion is to dissolve the unknown substance in water to which some ferrous sulfate has been added. Concentrated sulfuric acid is then added slowly, so as to form a layer below the aqueous solution. If a nitrate is present, a brown ring forms at the junction of the liquid surfaces. The test depends upon the formation of some nitric oxide, which combines with ferrous ions, forming a complex ion, FeNO^{++} , which has a brown color. Nitrites as well as nitrates produce the brown ring; so an additional test must be made. A nitrite will decolorize an acid solution of potassium permanganate, and a nitrate fails to destroy the color of a permanganate solution.

Aqua regia. The alchemists often wrote of aqua regia (royal water), so-called because it would dissolve gold. This liquid is made by adding one part of concentrated nitric acid to three parts of concentrated hydrochloric acid. Although neither of these acids will alone dissolve gold or platinum, the mixture readily does so. The strong solvent power of aqua regia is usually attributed to the action of chlorine, which is liberated in a reaction between the two acids.



NOCl is called nitrosyl chloride. It readily decomposes into nitric oxide and chlorine on heating.

Uses. Nitric acid is used in the manufacture of explosives, such as nitroglycerine, guncotton, trinitrotoluene (T.N.T.), and blasting gelatin. It is used also in the preparation of artificial silk, collodion, celluloid, and dyes. It is a solvent for metals like silver and copper. These metals dissolve only in acids that are oxidizing agents. A salt of nitric acid, potassium nitrate or saltpeter, is used in dry explosives, such as gunpowder, and in fire-

works. Sodium nitrate (Chile saltpeter) is used as a fertilizer. Silver nitrate is employed in medicine and in the preparation of the films, plates, and sensitized papers used in photography.

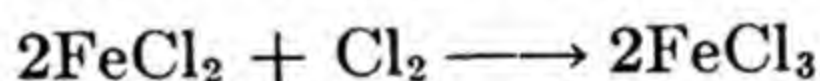
Questions and Exercises

1. A trace of nitric acid is sometimes found in rain water. Explain.
2. Pure nitric acid is colorless, but nitric acid obtained by distilling a nitrate with sulfuric acid is yellow. Explain.
3. Describe nitric acid and give one method for preparing it.
4. Mention two uses of nitric acid.
5. Write the formulas for the following: (a) nitric acid, (b) nitrous oxide, (c) nitrogen pentoxide, (d) nitric oxide, (e) nitrogen dioxide, (f) nitrous acid.
6. What is: (a) saltpeter, (b) Chile saltpeter?
7. Name two metals that will dissolve in nitric acid but not in hydrochloric acid.
8. How could you distinguish between the following gases? (a) oxygen and nitric oxide; (b) nitric oxide and nitrogen dioxide; (c) nitrogen and oxygen; (d) nitrogen and ammonia; (e) ammonia and nitrous oxide.
9. Compare the reactions taking place when NH_4NO_2 and NH_4NO_3 are heated. Write the equations.
10. Write an equation representing the burning of carbon in nitrous oxide.
11. What weight of oxygen is combined with 7 g. of nitrogen in each of the following compounds: N_2O , NO , N_2O_3 , NO_2 , N_2O_5 ? Do these compounds conform to the law of multiple proportions?
12. What weight of nitrogen is combined with 8 g. of oxygen in each of the following compounds: N_2O , NO , NO_2 , N_2O_5 ? Divide each of these different weights of nitrogen by the smallest of the four weights. Can the ratios be expressed in small whole numbers?
13. It has been estimated that the quantity of nitrogen gas converted into nitrogen compounds by lightning amounts to approximately 100,000,000 tons annually. The nitric acid formed in this way and carried to the soil by rain is soon converted into the salts (nitrates) that are required by growing plants. If all this acid were neutralized by limestone (CaCO_3), how many tons of calcium nitrate would be produced in the soil each year in this way?
14. What is the molecular weight of each of the oxides and acids of nitrogen?
15. What is the weight of a liter of each of the following gases measured under standard conditions: (a) nitrous oxide, (b) nitric oxide, (c) nitrogen dioxide?
16. Compare the density (weight of 1 liter) of each of the gases mentioned in Exercise 15 with the density of air.

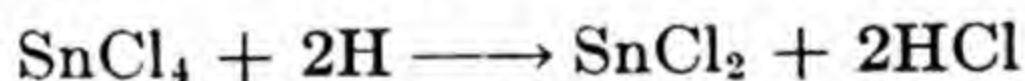
PART 4

Oxidation and Reduction

Most of the reactions which we have studied have involved no valence changes. Double-replacement reactions proceed without altering the valence of any atom. The neutralization of an acid by a base causes no change in the valences of the atoms or ions which take part in the reaction. On the other hand, chlorine acts upon ferrous chloride, converting it into ferric chloride, the valence of the iron atom changing from 2 to 3:



A reaction in which the valence of an atom is changed from any value to a higher positive value is an *oxidation* process. The reverse of this is *reduction*. When stannic chloride is mixed with zinc and hydrochloric acid (a hydrogen generator) the compound is *reduced* to stannous chloride.



We notice that in this case the valence of tin is changed from 4 to 2.

Although it is a common practice to connect oxidation and reduction processes with changes in *valence*, we shall make a slight modification of this practice and refer to the results of these reactions as changes in oxidation states. We shall, for example, say that the oxidation state of iron is changed from plus 2 to plus 3 when ferrous chloride is oxidized to ferric chloride. A free atom or molecule of any element will be regarded as in the zero oxidation state. The oxidation state of an atom corresponds to the electrical charge associated with the atom. In ferrous compounds the iron atom has two positive charges, Fe^{++} , and in ferric compounds three positive charges, Fe^{+++} . Uncombined iron atoms have no charge.

Earlier in the course we defined valence as the combining capacity of an atom. In many cases the combining capacity of an atom corresponds to the number of charges which the atom carries as an ion. This relation holds in the cases just cited. In ferrous chloride, for example, each iron atom holds two chlorine atoms, and

as an ion the atom has two positive charges. In ferric chloride each iron atom holds three chlorine atoms, and in the ionic state it has three charges, Fe^{+++} . In stannic chloride each tin atom has four positive charges and is able to hold four chlorine atoms, each having one negative charge. In stannous chloride each tin atom has two positive charges and is attached to only two chlorine atoms. In cases of this kind valence and oxidation states seem to mean the same thing, but there are other cases where they do not.

Let us look at the formulas of a few simple compounds of carbon. Marsh gas is CH_4 ; methylene chloride is CH_2Cl_2 ; chloroform has the formula CHCl_3 , and carbon tetrachloride is CCl_4 . What is the valence of carbon in CH_4 ? If we assign to hydrogen the valence of $+1$ we must say the valence of carbon is -4 (there must be an equal number of positive and negative charges in any neutral molecule).

Now examine the formula CH_2Cl_2 . If the valence of hydrogen is $+1$ and the valence of chlorine is -1 , then the valence of carbon becomes zero although we can see that it is in chemical combination with four atoms—two of hydrogen and two of chlorine. If chlorine has a valence of minus 1, then in CCl_4 the carbon atom has a valence of plus 4.

Let us now abandon the old plan of defining oxidation and reduction in terms of valence. Let us retain the term valence as a measure of *combining capacity*, that is, the number of bonds an atom forms with other atoms; and let us define oxidation as a loss of electrons or an increase in the positive charge on an atom. And we will define reduction as a gain of electrons or a decrease in the positive charge on an atom. We may summarize the results of this plan as follows:

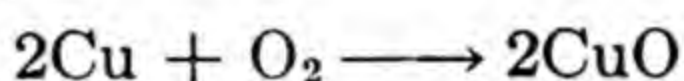
Formula of compound	Name of compound	Valence of first atom in the formula	Oxidation state of first atom in the formula
CH_4	Methane.....	4	-4
CH_2Cl_2	Methylene chloride.....	4	0
CCl_4	Carbon tetrachloride.....	4	+4
CHCl_3	Chloroform.....	4	+2
FeCl_2	Ferrous chloride.....	2	+2
FeCl_3	Ferric chloride.....	3	+3
SnCl_2	Stannous chloride.....	2	+2
SnCl_4	Stannic chloride.....	4	+4

The change from CH_4 to CCl_4 is an oxidation of the carbon atom which involves no change in valence. It is an oxidation

because chlorine atoms have a stronger tendency to acquire electrons than have hydrogen atoms. Neither CH_4 nor CCl_4 is ionized but in CCl_4 the four pairs of valence electrons are farther away from the carbon atom than they are in CH_4 . To a certain extent, therefore, the carbon atom has *lost electrons* and this is *oxidation*.

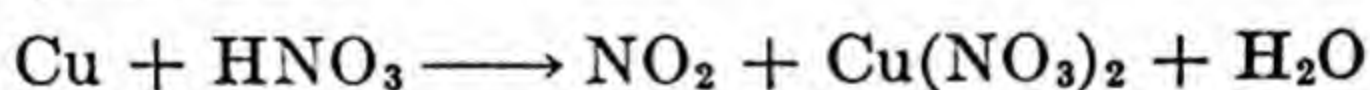
Oxidation-reduction equations. To balance any equation it is necessary to know the reagents used and the products formed. To balance an equation involving oxidation and reduction we must know also the changes in oxidation states (usually called changes in valence).

Consider a simple example first. Hot copper is oxidized by oxygen of the air to cupric oxide.

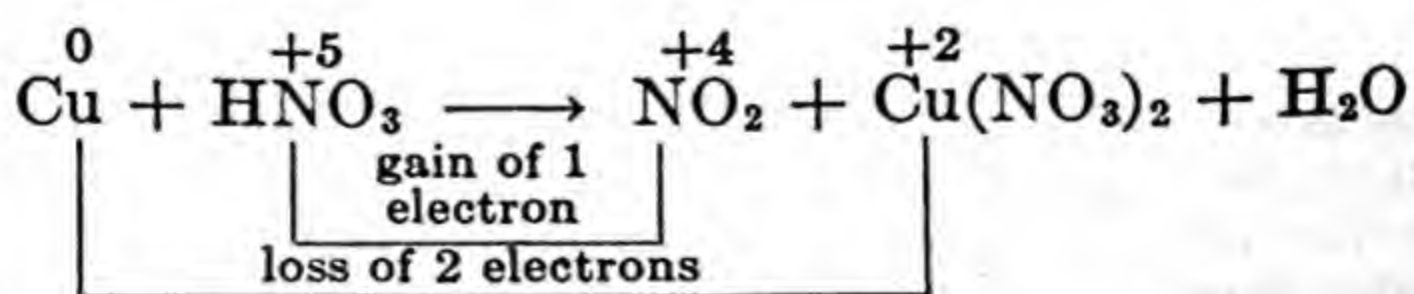


In this process the oxidation state of copper changes from zero to +2; and the oxidation state of oxygen changes from zero to -2. The copper has been oxidized (has lost electrons) and the oxygen has been reduced. Oxidation and reduction always go together. When one atom is oxidized (yields electrons) some other atom is reduced (accepts electrons).

The oxidation of copper by concentrated nitric acid is a more complicated process. The products formed are nitrogen dioxide, copper nitrate, and water. We first write the formulas for the reagents and products:



The oxidation state of the copper changes from zero to +2. The nitrogen atoms in the copper nitrate are still in NO_3 groups as they were in nitric acid. These atoms have not been oxidized or reduced. The nitrogen atom which appears in the form of NO_2 has been reduced. The oxidation state of nitrogen in HNO_3 is +5 and in NO_2 it is +4. We may indicate these changes as follows:

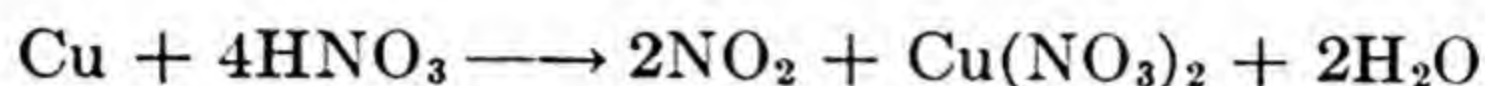


Since there must be as many electrons gained as lost we see that two molecules of nitric acid must be converted into NO_2 for every copper atom that reacts. Two additional molecules of HNO_3 are required to form the copper nitrate, $\text{Cu}(\text{NO}_3)_2$. Four molecules of nitric acid are accordingly required, of which two will be reduced to NO_2 and two will be used in forming the salt $\text{Cu}(\text{NO}_3)_2$.

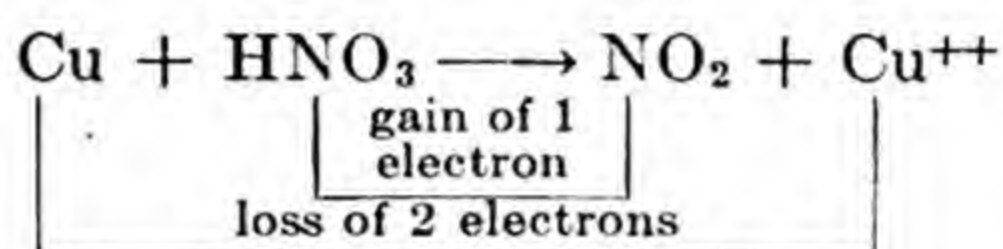
We may now rewrite the equation with these numbers inserted:



Inspection of this equation shows that balancing requires the addition of another molecule of water. The completely balanced equation is:



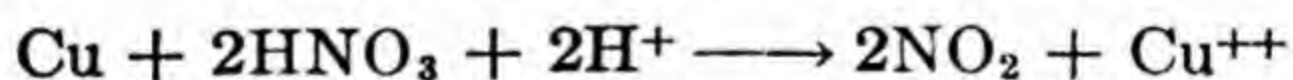
Let us approach the same problem in a little different way. We may limit our attention at first to the oxidation and reduction process, paying no attention to the formation of the salt and water. We have:



To balance the electrons lost and gained we must use 2HNO_3 and form 2NO_2 . We rewrite the equation:



This equation takes care of the electron exchange between the two substances entering into the reaction, but to be properly balanced, there must be the same net electrical charge on both sides of the equation. On the left side there are no charged ions. On the right side the copper ion carries a charge of $+2$. We must, therefore, either add two hydrogen ions to the left side of the equation, or two hydroxide ions on the right. These are the ions that enter into the formation of water. Since the solution is strongly acidic we know that hydroxide ions would not be among the products formed, but use of an excess of nitric acid would supply all the hydrogen ions we want. We balance the charges, therefore, by adding two hydrogen ions to the left side of the equation:



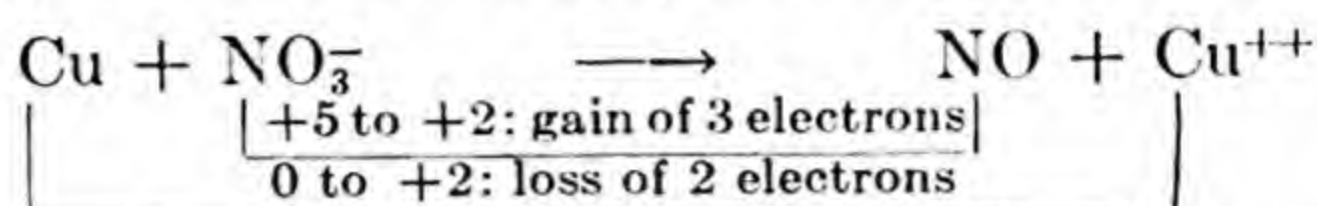
We have now taken care of the oxidation and reduction and we have balanced the charges. There remains only the addition of water on one side or the other to complete the equation:



This is the completely balanced equation for the reaction between copper and concentrated nitric acid. The other ions present, the nitrate ions, have not entered into the reaction in any way. They were there at the beginning of the reaction, and neither the nitrogen nor the oxygen atoms which they contain have changed in oxidation state. They may be entered in the equation if so desired,

but they do not take part in the oxidation or reduction process involved.

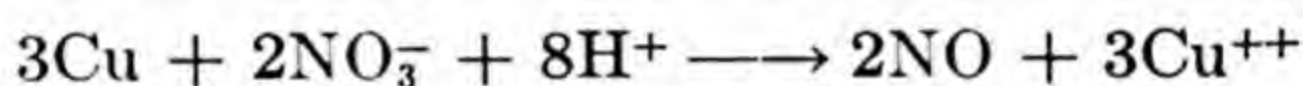
Let us balance the equation for a reaction between copper and a moderately dilute solution of nitric acid. As before, copper is changed to cupric ion, Cu^{++} , but this time the nitric acid is ionized and nitric oxide is the reduction product.



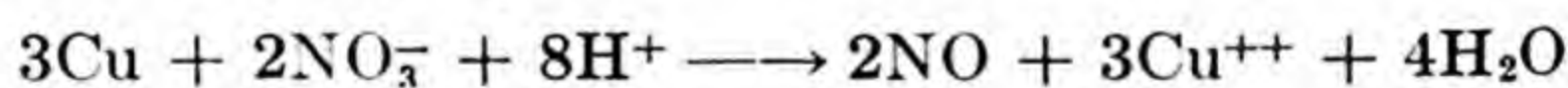
Two electrons are lost by each copper atom, and three electrons are gained by each nitrogen atom. To balance the electron exchange we must have three copper atoms and two nitrogen atoms:



The next step is to balance the charges on the ions. On the left side the charge is -2 and on the right side it is $+6$. We are not free to change the number of Cu^{++} ions or NO_3^- ions for the relative numbers now in the equation were established by the electron exchange. We are free to add more nitric acid and thus obtain hydrogen ions. If we add eight hydrogen ions to the left side of the equation the net charge will be the same on both sides.

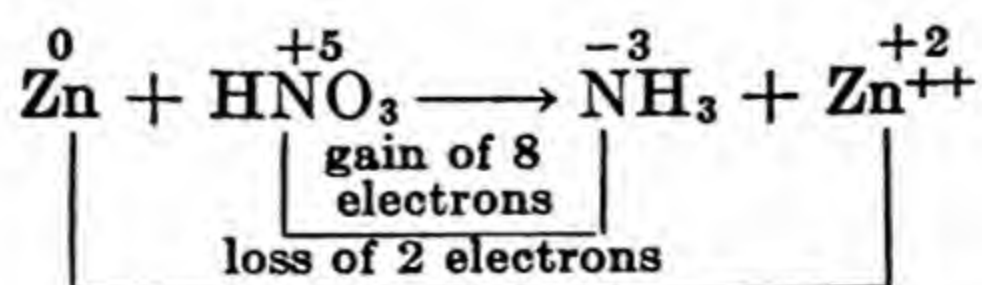


There remains only an adjustment to show the amount of water formed in the reaction:



The reaction between zinc and dilute nitric acid is more complicated, and it would be very difficult to balance the equation by a hit-and-miss method. Let us see what can be done with it in a systematic way. The products formed are zinc nitrate, ammonium nitrate, and water. Some of the nitric acid molecules are reduced to ammonia. The ammonia reacts with unchanged nitric acid to form the ammonium nitrate.

We first write the formulas for the reagents and the oxidation-reduction products:



The oxidation state of zinc is changed from zero to $+2$, a loss of two electrons. The oxidation state of nitrogen is changed from $+5$ to -3 , a gain of eight electrons. To balance this exchange

of electrons we must use four zinc atoms and one nitric acid molecule. The primary products will be four zinc ions and one ammonia molecule:



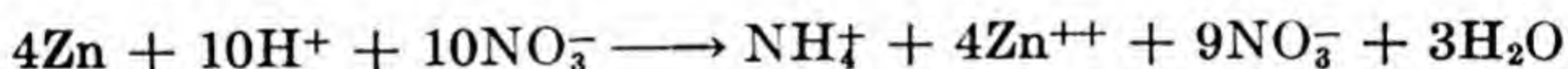
We now have eight positive charges on the right side and no electrical charges on the left side. To balance the charges we must use more acid which supplies H^+ ions. We need eight of these ions on the left side of the equation, and to balance the hydrogen and oxygen atoms we must place $3\text{H}_2\text{O}$ on the right side.



Since the hydrogen ions are supplied by nitric acid molecules, we could write 8HNO_3 instead of 8H^+ . We would then have eight NO_3^- ions to include among the products. Finally, remembering that ammonia would not exist in the free state in acid solution, we must add one more molecule of nitric acid to convert the ammonia into ammonium nitrate. We may then write the equation in either of the following forms:



Or



Questions and Exercises

1. When very dilute nitric acid reacts with zinc, a trace of nitrogen gas is formed. Write a balanced oxidation-reduction equation for the reaction, using nitrogen instead of ammonia as the reduction product.

2. When very dilute nitric acid reacts with magnesium, the main product is the ammonium ion, as in the case of zinc, but traces of nitrogen gas, N_2 , and nitrous oxide, N_2O , also are formed. Write the oxidation reduction equation for the reaction between magnesium and very dilute nitric acid, and assuming nitrous oxide to be the reduction product.

3. Write a balanced equation for the oxidation of hydriodic acid, HI , with concentrated sulfuric acid (see page 200).

4. Write a balanced equation for the oxidation of hydrobromic acid with concentrated sulfuric acid (see page 199).

5. Write an equation for the action of hydrochloric acid on manganese dioxide (see page 182).

6. When concentrated nitric acid acts on silver, silver ion and nitrogen dioxide are the products. Write the equation.

7. When moderately dilute nitric acid acts on silver, silver ion and nitric oxide are the products. Write the equation.

8. When concentrated nitric acid acts on magnesium, nitrogen dioxide, NO_2 , is the main reduction product of the nitric acid. Write the equation.

9. Which substance is oxidized, and which is reduced, when hydrochloric acid reacts with zinc?

PART 5

Speeds of Chemical Reactions

Many chemical reactions which we wish to carry out in the laboratory are too slow for practical purposes. We have learned that the yield of ammonia is greater at lower temperatures, but that the speed of the reaction is so slow at low temperatures that we would have to wait many years for the production of a usable quantity. It may be noted also that the hardening of a vegetable oil by hydrogenation is a very slow process if hydrogen gas is merely bubbled through the oil to be hardened. For a long time chemists have been concerned with the problem of causing reactions like these to take place faster and reactions like the rusting of iron, or the decay of wood, to proceed more slowly. Some of the methods for accomplishing these ends have been discussed, but we shall summarize them here.

The use of a catalyst. In the preparation of oxygen we learned that the presence of manganese dioxide in the tube of potassium chlorate causes a rapid evolution of oxygen at a comparatively low temperature. Manganese dioxide is a catalyst. The commercial process for the reaction between nitrogen and hydrogen to form ammonia is partly dependent upon the use of a catalyst. The presence of a finely divided metal like platinum or nickel causes the reaction between hydrogen and a liquid oil to be completed in a few minutes, instead of many years. Tons of commercial glucose are made annually from starch. When starch is heated with water and a little acid, the starch takes up some of the water and is transformed into a mixture of sugars. Without the acid catalyst, the rate of the reaction is too slow to be measured. Water is a catalyst for many reactions. There are common double-replacement reactions which will not take place at all in an absolutely dry state.

Substances which prevent a reaction from taking place are often called negative catalysts or inhibitors. A small amount of acetanilid, added to a solution of hydrogen peroxide, prevents its spontaneous decomposition into water and oxygen.

Temperature effects. Temperature has a marked influence on the speed of a reaction. Usually a reaction which takes place

slowly at a low temperature progresses rapidly at high temperatures. In order that two substances may react with each other, it is essential that their molecules come in contact, or collide, and they must possess certain minimum amounts of energy. An increase in temperature makes molecules move more rapidly, and this increases the number of collisions in a given time and increases also the force of each collision. It is found, experimentally, that an increase of $10^{\circ}\text{C}.$ in temperature usually doubles the rate of reaction between gaseous substances or between substances in solution.

Many applications of this principle are seen in everyday life. Plants grow very slowly in cold weather, but when the temperature rises, they grow rapidly. Fruits and vegetables ripen much faster when the weather is warm. Foods cook faster in a pressure cooker than in an open kettle, since the temperature of boiling water is increased by pressure. In the Haber process for making ammonia, a high temperature is employed to increase the speed of the reaction, and the speed is further increased by the use of a catalyst.

Conversely, we use refrigeration to slow down reactions which we wish to prevent. Milk sours more slowly in a refrigerator, and meat does not decay at low temperatures.

Concentration of the reacting substances. Any substance burns more rapidly in pure oxygen than in air. If a glowing splinter is plunged into liquid oxygen, it burns violently, because it is in direct contact with millions of oxygen molecules.

When pure hydrogen and oxygen gases are mixed at room temperature, the speed of the reaction between them is so slow that no appreciable amount of water would be formed in less than a million years. If, however, a small amount of powdered platinum or palladium is added to the mixture, the hydrogen accumulates on the surface of the metal until it reaches an enormous concentration. At this concentration the hydrogen molecules capture oxygen molecules so rapidly that the mixture takes fire spontaneously and the formation of water becomes instantaneous. We employ this same principle in order to capture a criminal who has escaped. If one man were sent to apprehend him, it might take a period of years for the two to come together. By sending a posse of 100 or more men, we shorten the time of the hunt.

Surface available for contact. If large granules of iron and sulfur are mixed together, they react slowly to form iron sulfide. If, however, the iron and sulfur are finely powdered and intimately mixed, the reaction proceeds rapidly.

Aluminum foil burns slowly in air, but if aluminum is ground into a very fine powder and blown into the air, a reaction similar to an explosion results when a spark is applied to the mixture.

Enzymes. There is a class of catalysts produced by living organisms, called enzymes. The zymase of the yeast plant, which catalyzes the formation of alcohol and carbon dioxide from sugars, and the ptyalin of saliva, which converts starch into sugar, are examples.

PART 6

Other Members of Group V

We have studied the properties of nitrogen, the first element in Group V of the Periodic Table. The other members of Group V—phosphorus, arsenic, antimony, and bismuth—resemble nitrogen in some respects, but there are many points in which they differ considerably.

Nitrogen is a gas, and phosphorus is a waxlike solid. Neither of these elements has metallic properties. Bismuth at the bottom of the group is decidedly metallic. Arsenic occupies an intermediate position in the group, and it has some metallic properties and some characteristics of nonmetals. On this account it is often called a *metalloid*. Antimony is more metallic than arsenic, but less so than bismuth.

This increase of metallic properties as we descend in any group of elements is characteristic of all groups of the Periodic Table. The most nonmetallic element usually heads the group, while the most metallic is found at the bottom.

Some properties of these elements are given in the table.

	P	As	Sb	Bi
Atomic weight.....	31.02	74.91	121.76	209.00
Atomic number.....	15	33	51	83
Isotopes.....	31	75	121, 123	209
Electron structure:				
1st shell.....	2	2	2	2
2nd shell.....	8	8	8	8
3rd shell.....	5	18	18	18
4th shell.....	—	5	18	32
5th shell.....	—	—	5	18
6th shell.....	—	—	—	5
Melting point, °C.....	44.1 White { 590 Red { (43 atmospheres)	{ 814 { (36 atmospheres)	630.5	271
Boiling point, °C.....	280°	610°	1440°	1420°

Phosphorus

Phosphorus was discovered by accident. A German alchemist, Brandt, was searching for the philosopher's stone with which he could transform other metals into gold. He evaporated a large volume of urine, mixed the solid residue with charcoal and sand, and heated the mixture. He was astonished to find a substance which glowed in the dark. He called it *phosphorus*, which means "bearer of light." This substance was later identified as an element.

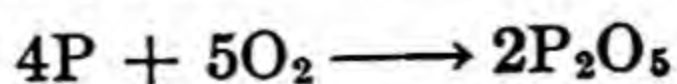
Occurrence. Phosphorus is too active chemically to be found free in nature. However, it occurs in many minerals, principally in the form of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. Large deposits of this substance are found in the United States and North Africa. Apatite, a compound of calcium phosphate and calcium fluoride, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$, occurs in large deposits in Canada and Russia. The bones and teeth of animals contain calcium phosphate. Plants contain small amounts of combined phosphorus, and animals have phosphorus compounds not only in the bony structure but also in the nerves and the brain.

Preparation. Phosphorus is obtained from phosphates by a process of reduction. Ground phosphate rock, silica, and carbon are mixed together in a furnace which is heated by means of a large carbon arc, and phosphorus distills out of the mixture:



The phosphorus, passing out of the furnace as a gas, is condensed to the liquid state by cooling, and it is then cast into molds, in which it solidifies. The molten calcium silicate is tapped off from the bottom of the furnace as slag. The process is carried out in the absence of air, since the phosphorus would ignite if oxygen were present.

Properties of white phosphorus. The phosphorus formed in this way is a soft, waxlike solid, which slowly turns yellow. Its melting point is 44.1°C . and it boils at 280°C . It is very reactive and combines readily with the oxygen of the air, forming P_2O_5 , a white solid called *phosphorus pentoxide*. Even at room temperature it combines with oxygen rapidly enough to produce visible white fumes of this oxide. At a slightly higher temperature it catches fire and burns with a brilliant flame:



Phosphorus is kept under water to exclude the air and; although its melting point is low, it must be melted under water to avoid

combustion. If a solution of phosphorus in carbon disulfide is poured on filter paper, the paper takes fire as soon as the carbon disulfide evaporates. The large surface exposed to the air causes rapid oxidation of the phosphorus. White phosphorus is *poisonous*.

Red phosphorus. Phosphorus exists in several allotropic forms, the most important of these being the white phosphorus just described, and a form called *red phosphorus*. If white phosphorus is heated in a retort from which air is excluded, red phosphorus is formed, heat being given out during the process. Hence red phosphorus contains less energy than white phosphorus, and is the stable form of the element at ordinary temperatures. White phosphorus, the unstable form, has a tendency to turn into red phosphorus, but the change occurs very slowly at room temperatures unless a catalyst is present. Iodine is a suitable catalyst. Exposure to light also accelerates the change. Sticks of white phosphorus are often coated with a layer of red phosphorus which has been formed from the white variety by light. Red phosphorus is a nonpoisonous powder which is insoluble in carbon disulfide. It is less reactive than the white form and does not have to be kept under water. When heated to a high temperature under atmospheric pressure, red phosphorus vaporizes without melting. The molecules of the vapor have the formula P_4 . When cooled the vapor condenses as white phosphorus. Red phosphorus melts at 590° if heated under a pressure of at least 43 atmospheres.

Matches. There are two types of matches on the market today: the kind which can be struck on any rough object, and the so-called safety match. The head of an ordinary friction match consists of a mixture of some substance which is easily kindled, usually phosphorus trisulfide, P_4S_3 ; some oxidizing agent, usually potassium chlorate, $KClO_3$, or barium chlorate, $Ba(ClO_3)_2$, to support the combustion of the kindling material; powdered glass to increase the friction; and glue to bind all of these substances together. Formerly, white phosphorus was used as the easily kindling substance, but its use was abandoned on account of its poisonous action upon the workmen in match factories. Phosphorus vapor entered the jawbones of the workmen through cavities in the teeth and attacked the bone until eventually the bone was entirely decomposed. A substitute for free phosphorus was found in the form of phosphorus sulfide, P_4S_3 . This compound, like phosphorus, is easily ignited, but unlike free phosphorus it does not injure the health of factory employees. Most countries now have laws prohibiting the sale of matches made with *free* phosphorus.

The head of the match is deposited on the end of a stick which has been coated with paraffin. When the match is scratched, the heat caused by friction raises the temperature of the surface sufficiently to ignite the mixture, and the phosphorus sulfide burns. The heat of combustion of the sulfide ignites the paraffin, and this latter in turn ignites the wood.

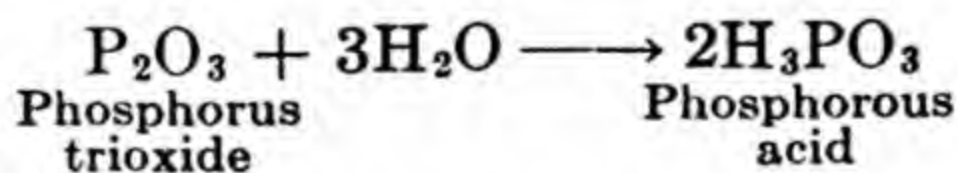
The head of the Swedish safety match contains antimony sulfide, Sb_2S_3 , an oxidizing agent, and glue. The surface of the box on which the match is struck is covered with red phosphorus, ground glass, and glue. Unless the safety match is struck on a specially prepared surface, the match does not ignite.

The manufacture of matches is now accomplished entirely by machinery. The wood splints are forced through a steel die from a wooden block of correct length. The splints protruding from the die are not punched out but are carried on a chain with many other units of the same kind through the various dips.

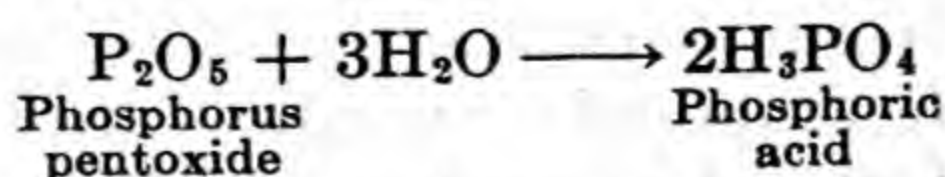
Compounds of Phosphorus

Phosphine (PH_3). This compound of phosphorus and hydrogen is analogous to ammonia, NH_3 . Like ammonia it is a gas, but it differs from ammonia in being very reactive, and when exposed to air it spontaneously catches fire and burns, forming H_2O and P_2O_5 . Phosphine is very poisonous.

Oxides. There are two common oxides of phosphorus. Phosphorus trioxide, P_2O_3 , is a white solid which is formed along with the pentoxide, P_2O_5 , when phosphorus burns in an atmosphere that does not supply enough oxygen to convert it completely into the pentoxide. The trioxide combines with water to form *phosphorous acid*:

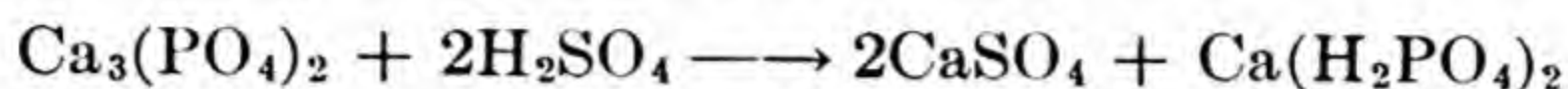


When phosphorus burns in oxygen or in an adequate supply of air, it forms the white solid pentoxide, P_2O_5 . The pentoxide has a very great affinity for water, and it is used extensively in chemical laboratories as a drying agent. On combining with water, it forms *phosphoric acid*:

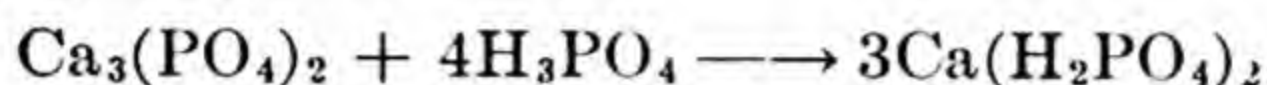


Phosphates. The most useful phosphate is the acid calcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$. This salt is used extensively as a fertilizer and as a component of some kinds of baking powder. Normal calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is a component of rocks

and mineral deposits in many localities, but it cannot be used as a fertilizer, for it is not soluble enough to be assimilated by plants. Treatment with sulfuric acid changes it to the acid phosphate, which is sufficiently soluble to be assimilated:



A phosphate fertilizer is made also by heating the insoluble calcium phosphate with phosphoric acid:



Phosphoric acid is made by heating calcium phosphate with a large excess of sulfuric acid:



The calcium sulfate formed in this reaction is relatively insoluble, and it precipitates.

Questions and Exercises

1. Describe the two forms of phosphorus and mention four differences in their properties.
2. What weight of phosphorus may be obtained from 50 lb. of tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$?
3. Devise a laboratory method for removing the water vapor from air.
4. How could you obtain pure red phosphorus from a mixture of the red and white forms of the elements?
5. How could you convert red phosphorus into white phosphorus?
6. The formula for phosphorus vapor is P_4 . What is its molecular weight?
7. How would you make a phosphate fertilizer from bones?
8. What materials are used in the manufacture of friction matches and safety matches?
9. Phosphine and ammonia are somewhat alike in their properties. Write the equation for the reaction between phosphine and hydrogen chloride. The product formed is called *phosphonium chloride*.
10. One liter of phosphorus vapor at 500°C . and 760 mm. will combine with how many liters of oxygen measured under the same conditions of temperature and pressure?

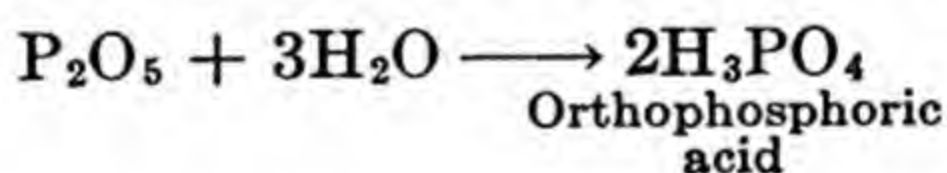
PART 7

Acids of Phosphorus

Phosphorus pentoxide is the anhydride of three acids. The difference between these acids depends upon the amount of water with which the anhydride is combined. They are known as orthophosphoric acid, H_3PO_4 ; metaphosphoric acid, HPO_3 ; and pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$.

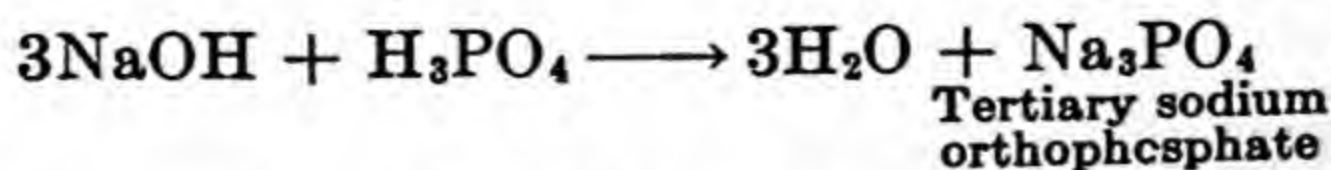
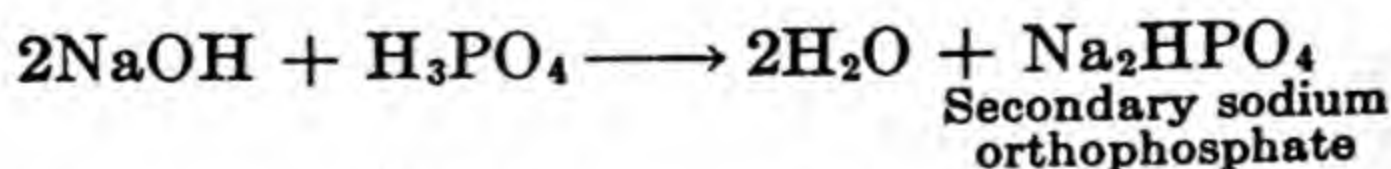
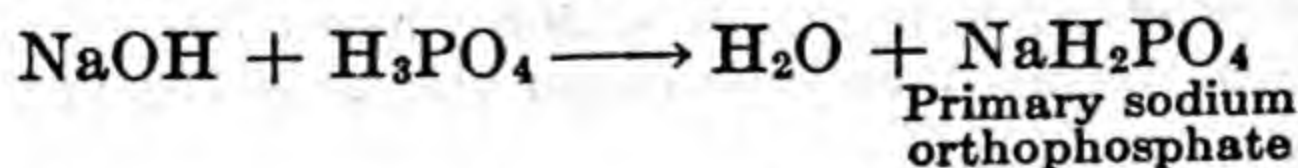
Phosphorus trioxide, P_2O_3 , is the anhydride of phosphorous acid, H_3PO_3 . There is another acid, hypophosphorous, having the formula H_3PO_2 . Its anhydride may be P_2O , but this oxide has not been isolated.

Orthophosphoric acid (H_3PO_4). This acid is formed when phosphorus pentoxide is dissolved in an excess of water:



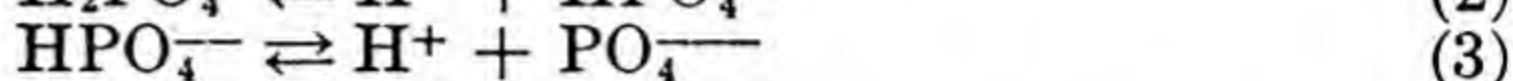
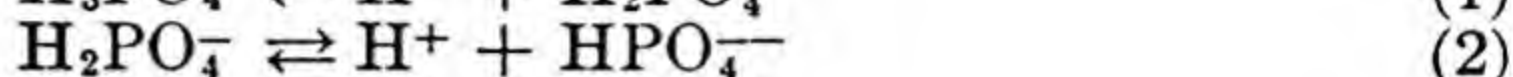
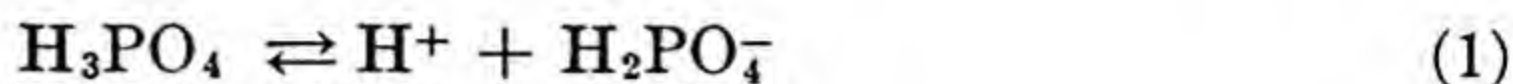
Phosphorus vapor is burned to P_2O_5 in a furnace similar to the one used in the production of phosphorus. The phosphorus pentoxide formed is then dissolved in water, and orthophosphoric acid is obtained in a pure condition. Another method for making it is shown on page 279.

Salts of orthophosphoric acid. Since orthophosphoric acid yields three hydrogen ions, it can form three types of salts, in which one, two, or all three of the hydrogen ions have been neutralized by the base. The following equations represent the reactions involved when the base employed is sodium hydroxide:



Tertiary sodium orthophosphate is often called *normal* sodium phosphate. All these sodium phosphates are used to remove boiler scale, and the normal salt is often used for softening water.

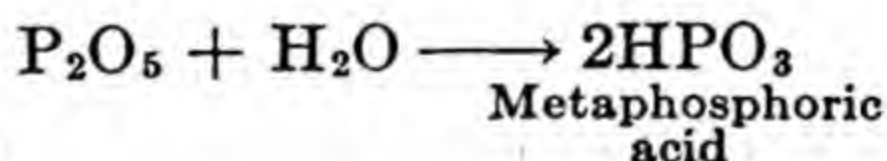
Ionization of orthophosphoric acid. Orthophosphoric acid can be neutralized in three steps. When it is dissolved in water, it ionizes as follows:



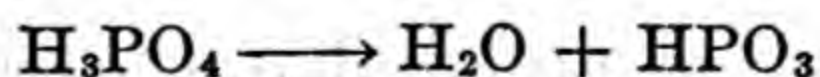
The ionization of H_3PO_4 according to equation 1 takes place to a considerable extent, although phosphoric acid is not as strong as hydrochloric acid. The tendency for H_2PO_4^- to ionize according to equation 2 is much less; hence there are few HPO_4^{2-} in a solution of orthophosphoric acid. The dissociation of HPO_4^{2-} into H^+ and PO_4^{3-} is negligible.

When a solution of a base like sodium hydroxide is added gradually to a solution of orthophosphoric acid, and methyl orange is used as the indicator, the color change appears when the hydrogen ions represented by equation 1 have been used up. The resulting salt is NaH_2PO_4 . If the addition of the base is continued, with phenolphthalein as an indicator, the hydrogen ions represented by the dissociation of the H_2PO_4^- (equation 2) can be neutralized, and the salt formed is Na_2HPO_4 . If the titration is continued until one more equivalent of the base has been added and the resulting solution is evaporated to dryness, the salt obtained corresponds to the formula Na_3PO_4 .

Metaphosphoric acid. When phosphorus pentoxide is exposed to moist air, a sticky, transparent substance is formed that looks like ice. It is often called "glacial" phosphoric acid, but it should be called metaphosphoric acid. Its formula is HPO_3 .

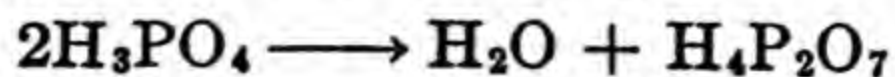


Metaphosphoric acid can be formed also by heating orthophosphoric acid to 400°C . This heating results in a loss of water by the orthophosphoric acid:



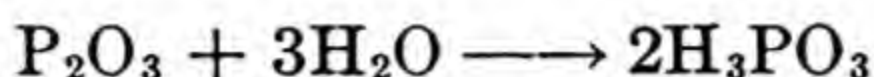
The sodium salt of hexametaphosphoric acid (see page 358) has found extensive use in laundries, since it prevents the precipitation of soap by calcium or magnesium ions in hard water.

Pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$). As its name implies, pyrophosphoric acid is formed by heating orthophosphoric acid for some time at about 250° :



Pyrophosphoric acid gradually changes back to orthophosphoric acid when it is dissolved in water.

Phosphorous acid. This acid may be prepared by dissolving phosphorus trioxide in cold water:

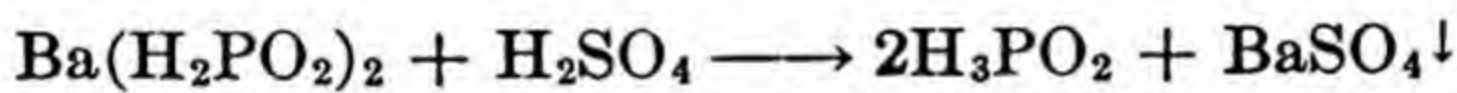


It is usually prepared, however, by the hydrolysis of phosphorus trichloride, with subsequent boiling of the solution until all of the hydrochloric acid is removed:



Phosphorous acid is obtained on cooling the solution. It is composed of white, deliquescent crystals, having an odor like garlic. It finds use as a vigorous reducing agent, readily precipitating metals like gold and silver from their salts. Its sodium salts, Na_2HPO_3 and NaH_2PO_3 are used as antiseptics and preservatives.

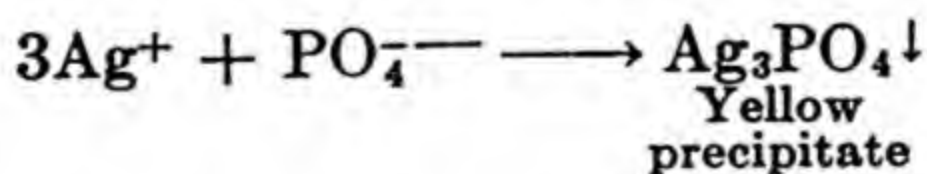
Hypophosphorous acid (H_3PO_2). The acid is generally prepared by treating barium hypophosphite with sulfuric acid:



Both the acid and its salts are powerful reducing agents. They are used frequently in medicine in the treatment of nervous diseases.

Other salts of phosphoric acid. There are many so-called mixed phosphates which are used in the laboratory. Two of these, microcosmic salt, $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, and magnesium ammonium phosphate, MgNH_4PO_4 , are used in quantitative analysis.

Tests for the various phosphates. Silver nitrate forms, with a neutral solution of phosphate ions, yellow silver phosphate:



Pyrophosphates and metaphosphates are both precipitated by silver ions in the form of insoluble white salts. We may distinguish between these two phosphoric acids by adding a solution of egg albumin to the acidified solution of the salt to be tested. Albumin is coagulated by metaphosphoric acid and not affected by pyrophosphoric acid. The test with silver ion is always applied to the salts, while the albumin test must be applied to the free acids. The solutions of the salts may be acidified with acetic acid for this purpose.

Orthophosphates may be detected by warming a nitric acid solution of the salt with ammonium molybdate. A yellow precipitate is formed if an orthophosphate is present.

If a solution of magnesium chloride, ammonium hydroxide, and ammonium chloride (magnesia mixture) is added to an orthophosphate, a white precipitate of magnesium ammonium phosphate, MgNH_4PO_4 , is formed.

Questions and Exercises

1. Write equations to show how you could make orthophosphoric, metaphosphoric, and pyrophosphoric acids from the element phosphorus.
2. Write equations for the preparation of metaphosphoric and pyrophosphoric acids from orthophosphoric acid.
3. How would you test a solution for the presence of the phosphate ion?
4. How might you distinguish between a solution of a metaphosphate and a pyrophosphate?
5. How many grams of sodium hydroxide would be required to react with 198 g. of orthophosphoric acid in order to make (a) primary sodium phosphate; (b) secondary sodium phosphate; (c) normal sodium phosphate?
6. How many grams of each salt would be formed in Exercise 5?
7. What is the percentage composition of magnesium ammonium phosphate?

PART 8

Arsenic, Antimony, and Bismuth

Arsenic

Occurrence. Arsenic usually is found in nature in the form of the sulfide, and is very often associated with copper ore. During the refining of copper, the arsenic sulfide is changed to arsenic oxide, which escapes with the flue gases. A few years ago it was regarded as a nuisance by copper refiners, but it is now in great demand for the manufacture of insecticides. Much of our supply of arsenic oxide comes from the cobalt mines in Canada. A gold-silver ore in Sweden contains 9 per cent arsenic and is the source of much of the world's supply. The United States produces annually approximately 25,000 tons of arsenic oxide.

Preparation. The pure element is easily obtained by heating arsenic oxide with carbon:



Properties. Arsenic occurs in several allotropic forms, as does phosphorus, but the common form is a steel-gray, very brittle solid with a metallic luster. It tarnishes easily and burns with a pale blue flame to form the oxide, As_2O_3 . It vaporizes when heated, and the vapor has a garliclike odor. The free element is not poisonous except in the vapor state, but the oxide is poisonous. In physical properties arsenic resembles the metals, but chemically it is a nonmetal, an acid former. Since it is in Group V, it has five valence electrons. In some of its compounds, for example As_2O_3 and H_3AsO_3 , it shares but three of these. In others, such as As_2O_5 and H_3AsO_4 , it shares all five.

Uses. The element is used in lead alloys in the manufacture of spherical shot. Shot is manufactured by allowing drops of molten lead to fall into water from a high tower. The drops of molten metal assume a spherical form and solidify in the descent. Arsenic increases the surface tension of the molten lead, giving each drop a greater tendency to assume a spherical form. Arsenic also hardens the lead.

Compounds. Arsine, AsH_3 , is a poisonous, colorless gas. The trioxide, As_2O_3 , and the pentoxide, As_2O_5 , are both white solids. Arsenic trioxide, often called arsenious oxide, is the anhydride of arsenious acid, H_3AsO_3 ; and the pentoxide, As_2O_5 , is the anhydride of arsenic acid, H_3AsO_4 . The salts of arsenic acid are called *arsenates*. Salts of arsenious acid are called *arsenites*. Lead arsenate, $\text{Pb}_3(\text{AsO}_4)_2$, and Paris green are used extensively as insecticides. Paris green is a double salt of copper acetate and copper arsenite, corresponding to the formula $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Cu}_3(\text{AsO}_3)_2$.

Of the domestic arsenic sold in the United States in 1941, approximately 68 per cent was used in insecticides, 19 per cent in weed killers, 2 per cent in wood preservatives, and 3 per cent in glass manufacture. Compounds of arsenic are used also in "dip" for sheep.

The Marsh test for arsenic. Chemists are called upon frequently to make analyses for arsenic. Compounds of arsenic are used as sprays for numerous orchard pests, and the amount that adheres to the fruit must be kept within certain limits.

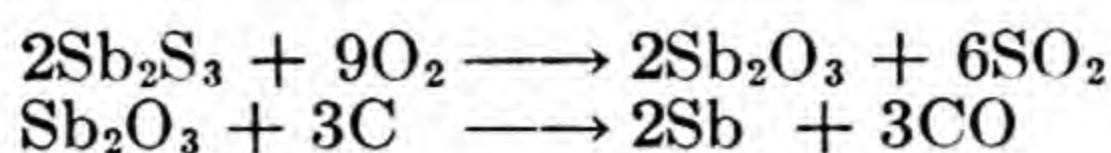
The test is usually carried out in the following manner: Hydrogen is generated by the action of dilute sulfuric acid on arsenic-free zinc. The hydrogen is dried by passing it through a tube containing calcium chloride. The calcium chloride tube is connected to a piece of hard-glass tubing which is drawn out to a point or jet. When all the air has been swept out of the apparatus the hydrogen is ignited at the end of the tube. The sample to be tested for arsenic is now introduced into the generator. If arsenic is present, it is converted into arsine, AsH_3 , in the generator, and passes out through the jet with the excess of hydrogen. If a piece of cold porcelain is placed in the flame, a lustrous, black deposit of arsenic forms on the cold surface.

A more delicate test, one which will detect as little as a millionth of a gram of arsenic, consists in heating strongly the hard-glass tube through which the mixture of hydrogen and arsenic is passing. The arsine is decomposed where the tube is heated strongly, and a mirrorlike deposit of arsenic is formed just beyond the heated portion of the tube.

Antimony

Occurrence. Antimony is found to a limited extent in the elementary state. The main source of the substance is the black sulfide, stibnite (Sb_2S_3). The world output of antimony is approximately 38,000 tons annually. China, Mexico, Bolivia, the United States, and Peru are the main producers.

Preparation. Antimony may be prepared by roasting stibnite in the air to the oxide, then heating the oxide with carbon:



Properties. Antimony resembles arsenic in its properties, but is more metallic. It is a brittle crystalline solid having a bright silverlike appearance. It is a poor conductor of heat and electricity.

Antimony reacts with sulfuric acid to form a sulfate of antimony. In this reaction the element plays the part of a metal. It also forms acids, where it acts like a nonmetal. Its highest valence is 5, although it often shares but three electrons.

Uses. When mixed with other elements, antimony has the property of making the alloy hard, and for this reason it is used in the manufacture of metal bearings. Antimony expands on solidifying—a property not displayed by other pure metals except bismuth. Other metals contract when the molten mass solidifies, and they draw away from the mold in which they are cast. In the manufacture of type metal, enough antimony is added to the lead to make the alloy expand very slightly on solidifying, and the type thus produced has the sharp corners necessary to print perfect letters and figures. Type metal thus produced also has the necessary hardness. Antimony also is contained in pewter and britannia metal. It is used in shrapnel shells and in bullets. A large amount is used in the form of lead-antimony alloy for plates in storage batteries. Plaster casts are given the appearance of steel by coating the cast with powdered antimony.

More of the world's supply of antimony is used in the United States than in any other country. Of this quantity, 65 per cent goes into the manufacture of automobiles. Large amounts are used also, alloyed with lead, as a cover for telephone cables.

Compounds of antimony find use in medicine and in the industries. Antimony chloride is used to give a dull finish to gun barrels. Antimony sulfide is used in the manufacture of red rubber goods, in making matches, and in producing a yellow tint in glass and porcelain. Antimony oxide is used in the manufacture of paint.

Bismuth

Bismuth is more strongly metallic than either arsenic or antimony, but its higher oxide, Bi_2O_5 , is weakly acidic.

Occurrence. Bismuth is less abundant than any other member of this family of elements. It is found chiefly in the uncombined form, but also occurs as the sulfide, Bi_2S_3 ; the oxide, Bi_2O_3 ; and

the telluride, Bi_2Te_3 . Most of the world's supply of bismuth comes from Peru and Canada, although some is being obtained from Nebraska, Indiana, and New Mexico in our own country. Bismuth is obtained from its ores by roasting, and then reducing the oxide with hot carbon.

Properties and uses. Bismuth has a metallic luster with a slight red tinge and, like antimony, it is crystalline and brittle, and it expands on solidifying. It melts at 271°C ., and some of its alloys have very low melting points. These low-melting-point alloys are used in automatic fire sprinklers. Water pipes in many large buildings are equipped with sprinklers which turn on automatically when the heat of the fire melts the alloy. The alloys are also used for automatic fire alarms which work on the same principle. Wood's metal melts at 71°C . It is composed of bismuth, 50 per cent; lead, 25 per cent; tin, 12.5 per cent; and cadmium, 12.5 per cent.

The commonest oxide of bismuth is the yellow solid trioxide, Bi_2O_3 . It is formed by burning bismuth in air.

Compounds of bismuth are used extensively in pharmaceutical preparations. Subnitrate of bismuth is used for the treatment of digestive disturbances, eczema, and ulcers.

Questions and Exercises

1. Name the elements of the fifth main group of the periodic system.
2. Why is arsenic called a metalloid?
3. Write the formulas of the anhydrides of the following acids: (a) phosphorous acid, H_3PO_3 ; (b) phosphoric acid, H_3PO_4 ; (c) sulfuric acid, H_2SO_4 ; (d) arsenious acid, H_3AsO_3 ; (e) arsenic acid, H_3AsO_4 .
4. Specify a commercial use for some arsenic compound.
5. Why is antimony used with lead in type metal?
6. Describe bismuth and mention one practical use of the metal.
7. How could you distinguish bismuth from arsenic?
8. What is an alloy?
9. Calculate the per cent of copper and of arsenic in Paris green.
10. Name the acids that are formed by dissolving the following anhydrides in water: N_2O_3 , P_2O_5 , and As_2O_5 .
11. How many pounds of arsenic could be obtained from 100 lb. of arsenic oxide?
12. Why is arsenic added to lead in making shot?
13. Why are arsenic compounds used as insecticides?
14. Write equations for the preparation of arsenic, antimony, and bismuth from their ores.
15. If 22.4 liters of arsenic vapor weighs 300 g. under standard conditions, what is the molecular weight of arsenic?

UNIT IX

Group IV of the Periodic Table: Carbon, Silicon, Titanium, Zirconium, Hafnium, and Thorium

PART 1

Carbon

Carbon and silicon are the most important members of the main family of Group IV of the Periodic Table. We shall consider them in detail.

The word "carbon" is familiar to all of us. Automobile owners speak of having the carbon removed from the valves in the engines of their cars. We guard against the danger of carbon monoxide poisoning, often caused by the exhaust fumes from our cars. We drink "carbonated waters" for refreshment. We ventilate our rooms to avoid an accumulation of carbon dioxide, which is exhaled in the breath. The element carbon, the first one in Group IV of the Periodic Table, is one of the most widely distributed elements in nature.

Occurrence. Carbon is found in nature both as the free element and in combination with other elements. The diamond is practically pure carbon. Graphite is almost pure carbon, but it differs from the diamond in crystalline form. Diamond and graphite are two different crystalline forms of the same element. They possess different physical properties, and they are said to be *allotropic* forms of carbon (see page 50). Although the two substances differ greatly in appearance, we know that they are both carbon, because when they are burned, carbon dioxide is the only substance formed. Carbon exists also in many *amorphous* or noncrystalline states, the commonest of these being charcoal, lampblack or soot, and coke. Anthracite coal is approximately 90 per cent carbon, and soft coal is 60 per cent to 80 per cent carbon.

More than half of the compounds that exist contain carbon as one of the elements in the molecule. When we exhale, carbon dioxide passes from our lungs. Natural gas, which is used as a

fuel in many parts of our country, is composed of compounds made of carbon and hydrogen. Gasoline, kerosene, and the oils we use in our automobiles also are composed of carbon and hydrogen. Whole mountain ranges are composed of limestone, which is chiefly calcium carbonate, CaCO_3 ; and in combination with oxygen, hydrogen, nitrogen, and some other elements, carbon is found in every living cell of all plants and animals.

PHYSICAL PROPERTIES OF CARBON

Atomic weight.....	12.010	Density:	
Atomic number.....	6	Diamond.....	3.51
Isotopes.....	12, 13	Graphite.....	2.25
Electrons in shells:		Melting point, °C.....	3500
1st shell.....	2	Boiling point, °C.....	4830
2nd shell.....	4		

All varieties of carbon are odorless and tasteless solids. Carbon is insoluble in water, and it has the highest melting point of all the elements. When subjected to the high heat of the electric arc, carbon vaporizes to a slight extent but does not melt. The older type of electric light bulb contained a carbon filament—a thin thread of carbon which withstood for some time the tremendous heat required to make it glow and produce light. Tungsten, which vaporizes to a lesser extent than does carbon, is used in our modern electric light bulbs.

Chemical properties. Carbon has a great tendency to combine with oxygen at moderate temperatures, forming carbon dioxide or, with a limited supply of oxygen, carbon monoxide. It will take oxygen away from many other elements; hence it is a good deoxidizing, or reducing, agent. Carbon is not acted upon by acids, bases, or other ordinary chemical reagents.

Crystal forms of carbon. Most of the diamonds in the world come from mines located in Brazil, Borneo, India, and South Africa. Diamonds do not appear bright and attractive when taken from the earth, for they are covered with a crust of dark mineral matter. The stone cutter removes this dark layer, then cuts the crystal to a form that insures the maximum reflection of light. A properly cut and polished diamond possesses unrivaled brilliance and is one of the most highly prized gems.

The Cullinan diamond, the largest diamond ever found, was obtained from a mine in South Africa in 1905. It weighed 3025 carats before it was cut. A *carat* is almost 0.2 g. Not all diamonds possess the white brilliance of the stones to which we are accustomed. Some are dark and have no value as gems.

Since the diamond is the hardest naturally occurring substance known, it is used in tools for cutting glass and as a point for drills used for cutting hard rocks. The density of diamond is 3.5 g. per cubic centimeter. It is hard and brittle, and it is not attacked at ordinary temperatures by any chemical reagent. When heated in air or oxygen, it burns—the only product formed being carbon dioxide.

Many chemists have tried to make diamonds in the laboratory. It is known that in the diamond the atoms are closer together than in any other form of carbon. If we subject hot carbon to a very high pressure, will we force the atoms closer together and in this way make diamonds? A French chemist, Moissan, tried the experiment. He saturated molten iron with carbon, then plunged the molten mixture into water to form a crust of solid iron around it. The interior of the mass was then allowed to cool slowly. Molten iron which is saturated with carbon expands as it cools. The solid shell produced by suddenly cooling the outer layer prevented expansion inside, and the result was the development of a high pressure in the interior of the mass. Under these conditions many tiny crystals of diamond were formed. The iron was dissolved in hydrochloric acid, and the very small diamonds were found in the insoluble residue. Most of them were microscopic, and none had a diameter greater than 0.5 mm. Larger diamonds could not be made by repeating the experiment on a larger scale. Most of the carbon which was recovered from the iron was in the form of graphite.

Graphite. Graphite is found in natural deposits in many places, particularly in Siberia and Ceylon. Perfect crystals of graphite are rare. It is a soft, black, lustrous substance with a greasy feeling. Its density is about 2.2 g. per cubic centimeter. It is used to protect iron from rusting. Ordinary stove polish contains graphite. It is used as a lubricant in many types of machines, and it is especially useful where wooden bearings move upon each other. Fine particles of graphite fill all the crevices of the wood and provide smooth surfaces that move over each other with little friction.

Graphite is made commercially at Niagara Falls, where electric power is cheap. The method employed is to heat anthracite coal to approximately 3000°C . in an electric furnace. Carbon sublimates at this temperature; that is, it passes into the vapor state and resolidifies without melting. When carbon vapor returns to the solid state, it is in the form of graphite.

Because of its resistance to the action of chemicals and heat, and also on account of its capacity to conduct a current of elec-

tricity, graphite is used extensively in the electrical industries in making electrodes for arc lamps and for electric furnaces. It is mixed with clay to form the slender rods that are used in the manufacture of pencils, misnamed "lead" pencils.

Amorphous Forms of Carbon

Coal. Coal is a form of fossilized wood—wood that has lain buried under tons of soil for many centuries. There was a time in the history of the earth when climatic conditions promoted a luxuriant growth of trees, ferns, and other plants of all kinds. This period is known as the Carboniferous Age. During that period, in certain regions not far above the level of the sea, vegetable matter accumulated in enormous quantities. Vegetable matter is composed largely of compounds of carbon, hydrogen, and oxygen. This material was later covered by mud, sand, and water. When buried to a considerable depth it was under great pressure and, at the same time, it was subjected to the heat from the interior of the earth. Under these conditions volatile products, containing hydrogen and oxygen, gradually escaped, and the remainder, composed chiefly of carbon, formed the coal seams of the earth. Coal retains the cellular structures of the plants from which it was derived. These structures can be seen by examining a thin layer of coal with the aid of a microscope. In soft coal the fossil remains of leaves and stems of plants can be seen without a microscope. Trees have been found that are only partially carbonized, one end being coal and the other still wood.

Varieties of coal. There are several kinds of coal, and these differ from each other in the amount of disintegration which has taken place. Anthracite coal is a hard, dense, shiny coal which is more than 80 per cent carbon. Most of the hydrogen and oxygen have been driven out of the wood from which this coal was made. Anthracite burns slowly, with practically no flame and without the formation of soot. It is, therefore, the most desirable kind of coal to burn in a furnace or stove.

In bituminous or soft coal, the decomposition has not proceeded as far as in anthracite coal. Some of the carbon is still combined with hydrogen in the form of compounds called *hydrocarbons*. These have a high heat content, but burn with a smoky flame, producing soot. Bituminous coal also contains compounds of nitrogen and sulfur.

Lignite contains more hydrogen compounds of carbon than does bituminous coal. It shows much of the structure of the wood from which it was formed.

Peat is a brown mass of moss and leaves which has undergone, to a slight extent, the same change by which coal is formed. It is usually found in bogs, saturated with water. It must be dried before it can be used as fuel.

Wood charcoal. When wood is heated in the absence of air, gaseous and liquid products distill out, and charcoal remains in the retort. Among the volatile liquids driven out of the wood are methyl alcohol, acetone, and acetic acid. These are three valuable liquids. They are used in enormous quantities in the chemical manufacturing industries, and prior to 1925 the distillation of wood for the production of these liquids was a profitable business. All these compounds are now made by chemical processes that are much cheaper than the process of distilling wood. Wood alcohol (methanol), acetic acid, and acetone are not present as such in wood, but are formed from the components of the wood during the heat treatment. The wood is heated in large iron chambers called *retorts*. The process of decomposing a substance by heating it in the absence of air is called *destructive distillation*. Air is kept out of the apparatus so that the wood will not take fire.

Charcoal has the property of holding on its surface large quantities of gases. The layer of gas that clings to a solid surface is said to be *adsorbed*. Charcoal is very porous, and the surface area presented by a single cubic inch of the substance may amount to hundreds of square feet. On account of its power to adsorb gases, charcoal has been used in gas masks. Charcoal clings also to small particles of solid substances. Water which has been colored by indigo may be decolorized by passing it through a charcoal filter. The dye particles are retained on the surface of the charcoal. Bacteria may be removed from water in the same way, but there is a limit to the capacity of charcoal to hold these things, and the filters become ineffective unless the old carbon is replaced frequently by fresh material.

Coke. Bituminous coal is converted into coke by a process quite similar to the conversion of wood into charcoal. When coal is heated in a retort, several different gaseous and liquid products are expelled. Some of the gases that escape are combustible and they are used for fuel. Ammonia is one of the compounds formed in the destructive distillation of coal. Ammonia gas is very soluble in water and can be separated from the fuel gases (carbon monoxide, methane, and hydrogen) by passing the mixed gases through water. Ammonia is more completely removed from the fuel gases by passing the mixture through sulfuric acid. The ammonia combines with the acid, forming ammonium sulfate.

The fuel gases escape unchanged, for they do not react with sulfuric acid.

From the liquid and tarry distillation products of coal we obtain benzene, phenol, and many other valuable compounds. The solid residue—coke—is about 90 per cent carbon and 10 per cent mineral matter. The latter appears in the ash when coal or coke is burned. Coke is a porous, gray substance having a high heat value. It is used in enormous quantities in smelting ores. It not only serves to heat the ore but acts as a reducing agent, liberating metals from the ores, which usually are oxides. At a high temperature iron oxide is reduced by carbon, as indicated by the equation:



Coke is superior to coal for this purpose, since it contains much less sulfur to contaminate the metal.

Boneblack. Animal charcoal, or boneblack, is made by heating bones in a vessel from which air is excluded. It is only about 10 per cent carbon, but this carbon is in the form of very fine particles and is distributed through a porous mass of mineral matter. It is used to decolorize and clarify solutions containing colored matter and suspended particles of any kind. Such substances are adsorbed by the carbon.

Lampblack. Soot or lampblack is made by burning kerosene or turpentine with a supply of air insufficient to convert all the fuel into gaseous products. It is used in the manufacture of printer's ink, black paint, and rubber.

Questions and Exercises

1. Name five forms in which carbon exists in the free state.
2. Name the uses of each of these forms.
3. What is meant by the term "allotropic form"?
4. In what way does amorphous carbon differ from other allotropic forms of the element?
5. Would you say that anthracite coal has been undergoing carbonization for a longer or shorter time than bituminous coal? Explain your answer.
6. Why are fence posts often charred before being placed in the ground?
7. Are all diamonds valuable? Explain your answer.
8. The allotropic forms of carbon are very different in appearance. How could you prove that diamond, graphite, lampblack, and anthracite coal are all forms of the same element?
9. Which is the best form of coal for household use? Why?
10. Would peat be a satisfactory fuel for use in a fireplace?

11. Why is graphite, instead of any one of the other forms of carbon, used in batteries?

12. Why is a piece of charcoal a better substance for adsorbing gases than a piece of anthracite coal of the same size?

13. Name three uses for graphite.

14. Printer's ink is made of lampblack. Could it be bleached by means of chlorine?

15. What kind of paint would you use for covering the inside of a drum in which an acid or a base was to be stored?

16. Name some of the common compounds of carbon that occur in nature.

17. What is meant by the "destructive distillation" of wood? What product remains in the retort?

18. What products are formed in the destructive distillation of coal?

19. What form of carbon is used in gas masks? Why?

20. What is used as "lead" in "lead pencils"?

PART 2

Oxides and Acids of Carbon

Carbon Monoxide

Occurrence and properties. When carbon burns in a limited supply of air, a colorless, odorless gas called *carbon monoxide* (CO) is formed. Carbon monoxide is inflammable, and burns with a pale blue flame. All of us who have seen a coal fire in a furnace or fireplace have seen the blue flame of carbon monoxide near the top of the coal. As the flames and heated air rise, cold air is rapidly drawn in around the bottom of the burning coal. This supplies a sufficient amount of oxygen to convert the lower layer of the coal to carbon dioxide. As this gas rises through the pile of hot, unburned coal, the carbon partially reduces the carbon dioxide; that is, it takes away one atom of oxygen from each molecule of carbon dioxide, leaving carbon monoxide:

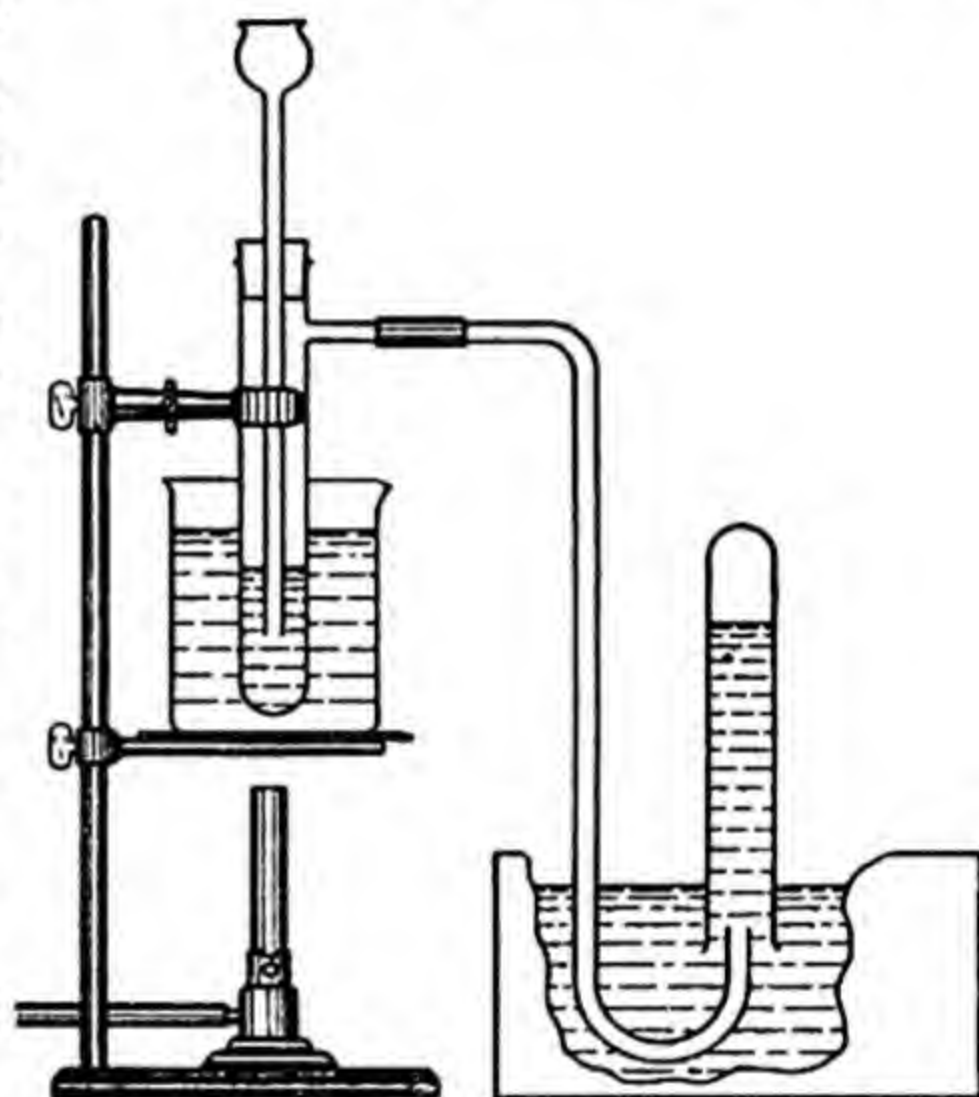
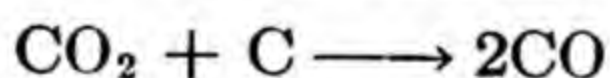


Fig. 133. A carbon monoxide generator.

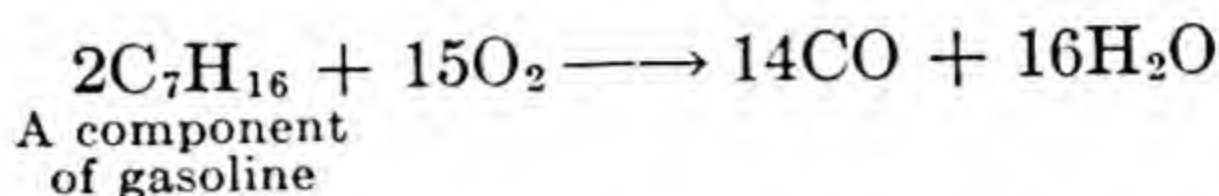
When this carbon monoxide reaches the top of the pile of coal, where there is again a good supply of air, it burns with its characteristic blue flame to carbon dioxide.

If the supply of air in the furnace is not sufficient to complete this reaction, some carbon monoxide may escape into the building. Carbon monoxide is a very poisonous gas, and a small amount of it in the air causes illness or death.

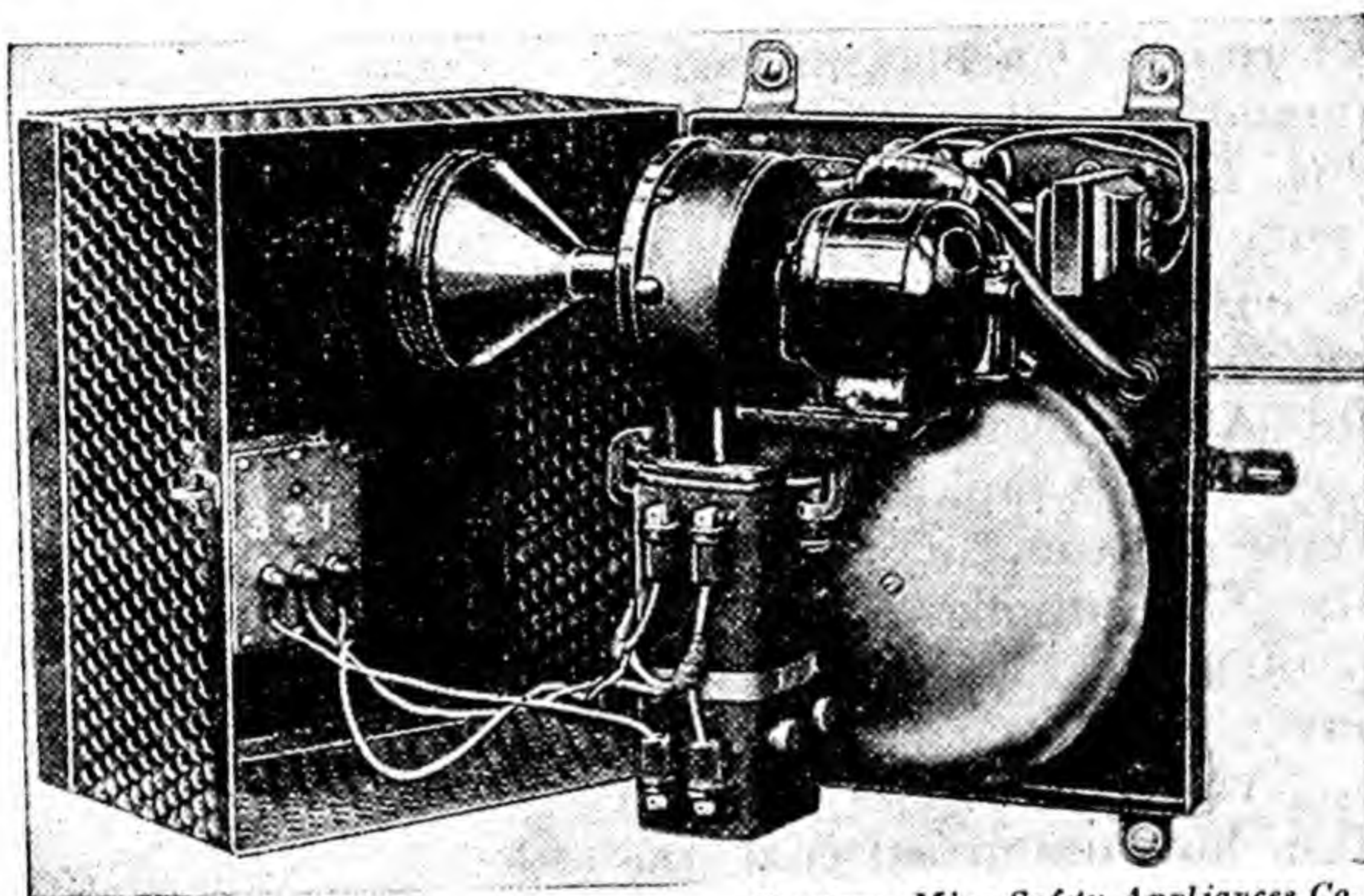
Carbon monoxide is poisonous because it combines with the hemoglobin in the blood, making these red cells incapable of combining with oxygen. Death follows the formation of much of this compound in the blood stream.

Carbon monoxide is also one of the products of combustion when fuels containing carbon (wood, coal, gasoline, and so forth)

burn in a supply of air that is not sufficient to convert the carbon part of the fuel entirely to carbon dioxide. In an automobile engine most of the gasoline is burned to carbon dioxide and water, but a little carbon monoxide is formed:



This reaction is one of those that take place in an automobile engine. The carbon monoxide goes into the air with other exhaust



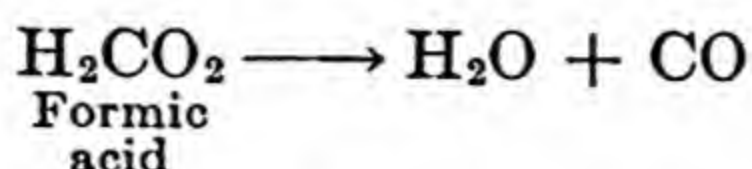
Courtesy, Mine Safety Appliances Co.

Fig. 134. A carbon monoxide detector. A sample of air is drawn through the apparatus. Half of the air goes through a chamber containing a catalyst which causes any carbon monoxide present to burn to carbon dioxide. The other half of the air goes through a similar chamber containing no catalyst. The difference in temperature in the two chambers causes the bell to ring.

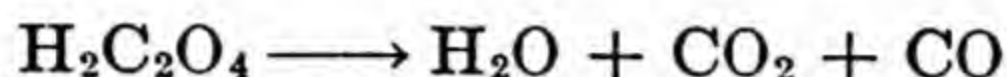
fumes of the engine. The exhaust gas sometimes contains as much as 12 per cent of the poisonous gas, though it usually holds only 3 or 4 per cent. Many deaths occur every year as a result of allowing automobile engines to run in closed garages.

A person may be poisoned by sitting in a closed car in which the engine is left running. The exhaust gases penetrate through the floor boards of the car, causing death before the presence of the dangerous gas is even suspected. Whenever an automobile engine is running, there should be a good circulation of air both inside and outside the car.

Laboratory preparation. Carbon monoxide is usually prepared in the laboratory by removing water from formic acid, H_2CO_2 . Concentrated sulfuric acid is used as the dehydrating agent:

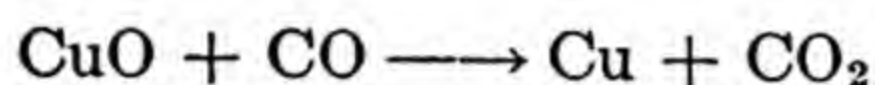


It may be prepared also by heating oxalic acid with concentrated sulfuric acid:



The carbon dioxide is easily separated from the carbon monoxide by passing the mixed gases through a solution of sodium hydroxide. (This reaction is explained on page 170.)

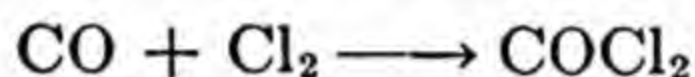
Reducing action of carbon monoxide. We have already studied the reducing action of hydrogen on metallic oxides. Carbon monoxide acts in a similar manner. It reduces copper oxide to copper:



It acts also on iron oxide, forming iron and carbon dioxide:



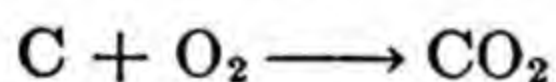
Phosgene. Carbon monoxide and chlorine combine to form a poisonous gas known as *phosgene*, which has the formula COCl_2 :



The reaction is catalyzed by light or by contact with charcoal.

Carbon Dioxide

Occurrence. When carbon burns in air, an odorless, colorless gas is formed which is called carbon dioxide:



Carbon dioxide is formed also when compounds of carbon burn in a large supply of air. Wood yields carbon dioxide and

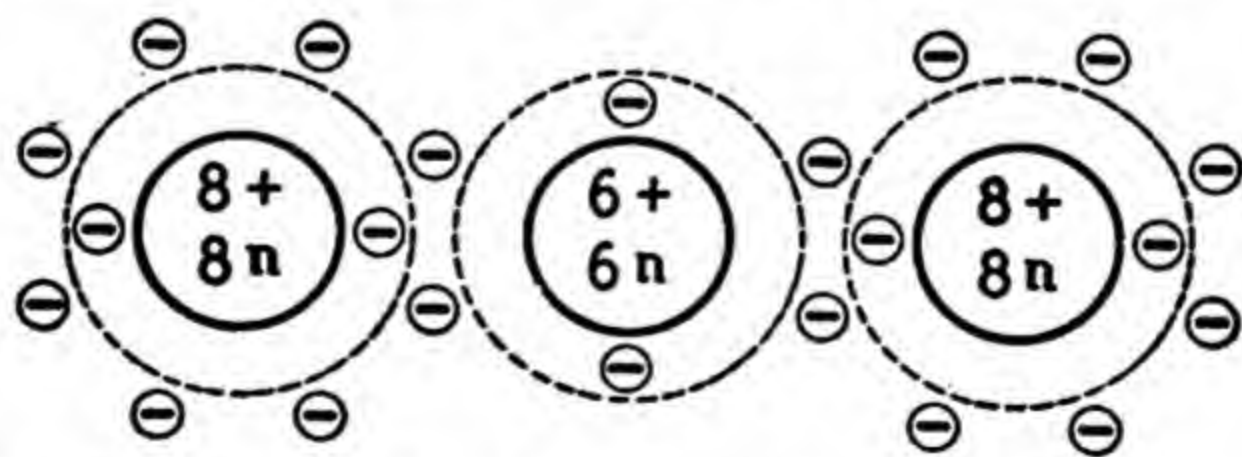
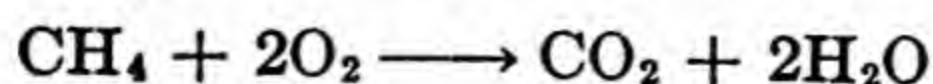
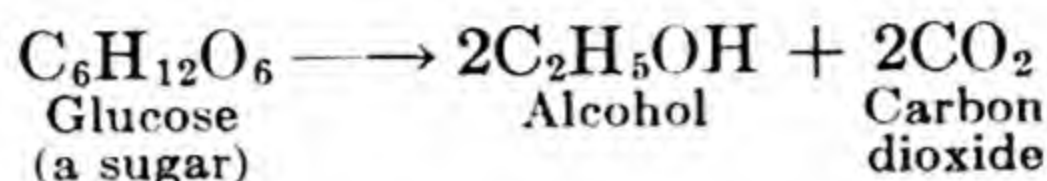


Fig. 135. Carbon dioxide molecule—diagrammatic. Actually, two additional electrons from each oxygen atom are shared with the carbon atom.

water. Natural gas, which is burned as fuel in many of our cities, is composed largely of methane, CH_4 . The burning of methane also produces carbon dioxide and water:



Carbon dioxide is formed in the fermentation process by which a sugar is converted into alcohol. When yeast is added to a solution of cane sugar or of glucose, carbon dioxide is produced at a slow but steady rate:

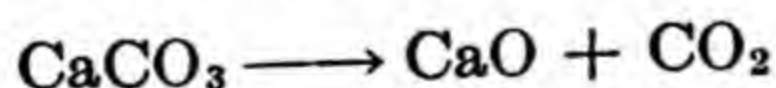


The decay of plant and animal matter furnishes carbon dioxide to the air, as does every breath exhaled by every living animal. The gas is produced by volcanoes and by some springs, called "soda springs," the water of which is charged with carbon dioxide. Small bubbles of the gas may be seen escaping from the water in such springs.

Carbon dioxide and the oxygen cycle. Although carbon dioxide is being poured into the air continually, there are actually only about 300 parts of the gas in 1,000,000 parts of air. Where, then, does it go? Why has not all of the oxygen been removed from the air long ago and its place taken by carbon dioxide? The answer is that plants use carbon dioxide as part of their food. When the sun shines on the green coloring matter in the leaves of the plant, carbon dioxide, taken from the air, and water, absorbed through the roots, are changed to starch, cellulose, and other compounds which are stored in the plant. At the same time oxygen is returned to the air. Thus the plants and animals work together to make the atmosphere a place in which both can survive.

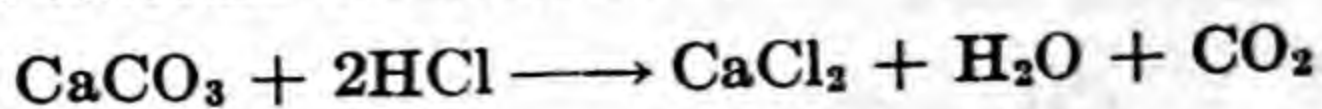
Preparation of carbon dioxide. Many tons of carbon dioxide are used each year for charging water. Carbon dioxide under pressure is forced into water in the process of making so-called soda water. A large amount of the carbon dioxide used for this purpose is made by burning anthracite coal in air, and purifying the carbon dioxide evolved.

Sometimes carbon dioxide is made for commercial use by heating limestone, which is impure calcium carbonate:



Lime, CaO , is a valuable by-product of this reaction.

A convenient laboratory method for making the gas is shown in Fig. 136. Small pieces of marble are placed in a flask, and dilute hydrochloric acid is then added from a dropping funnel. The carbon dioxide gas evolved is conveyed by a delivery tube to a bottle, in which it is collected by displacement of air. Marble is nearly pure calcium carbonate.



Physical properties of carbon dioxide. Carbon dioxide is slightly soluble in water. We therefore lose some of the gas when it is collected by the displacement of water. It is considerably heavier than air, and can be collected easily by the

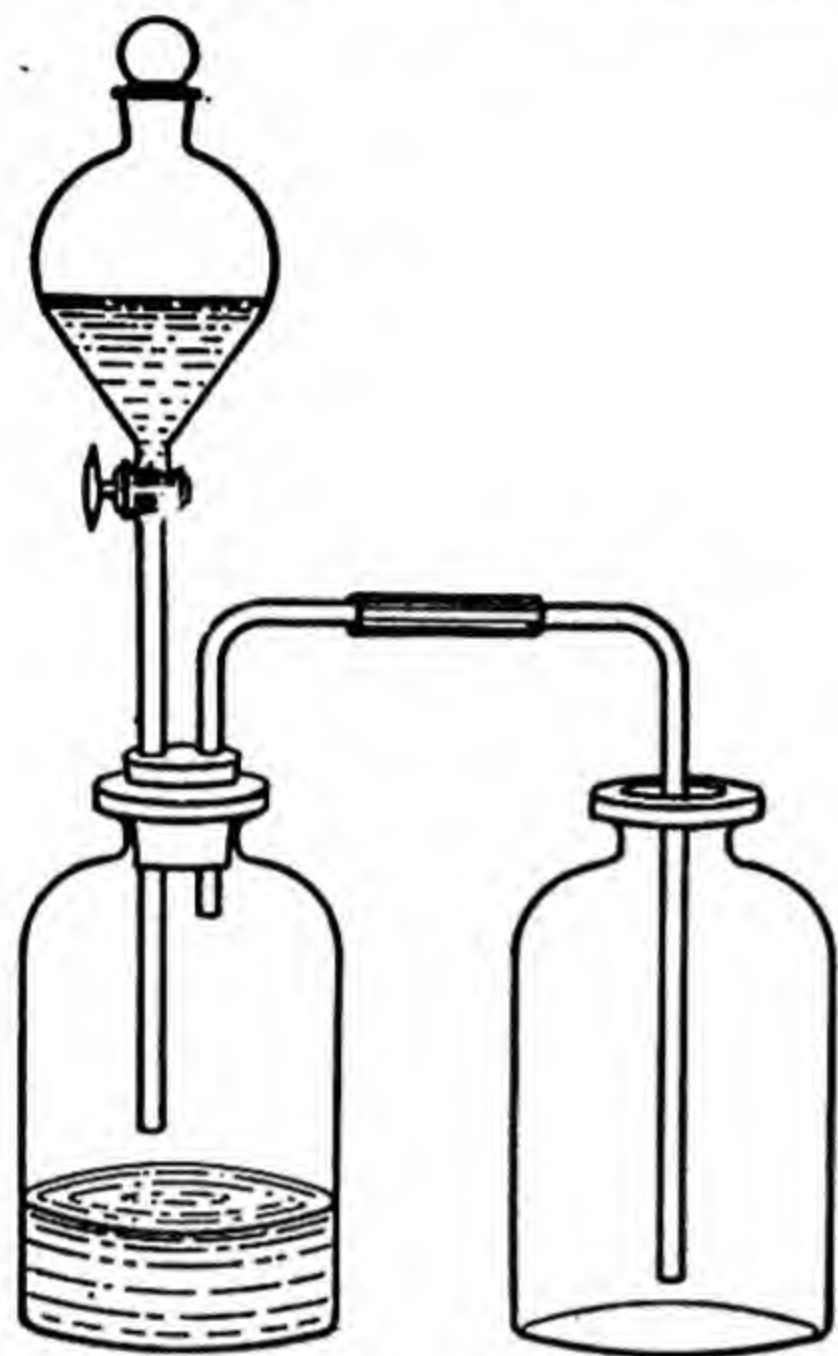


Fig. 136. Preparation of carbon dioxide.

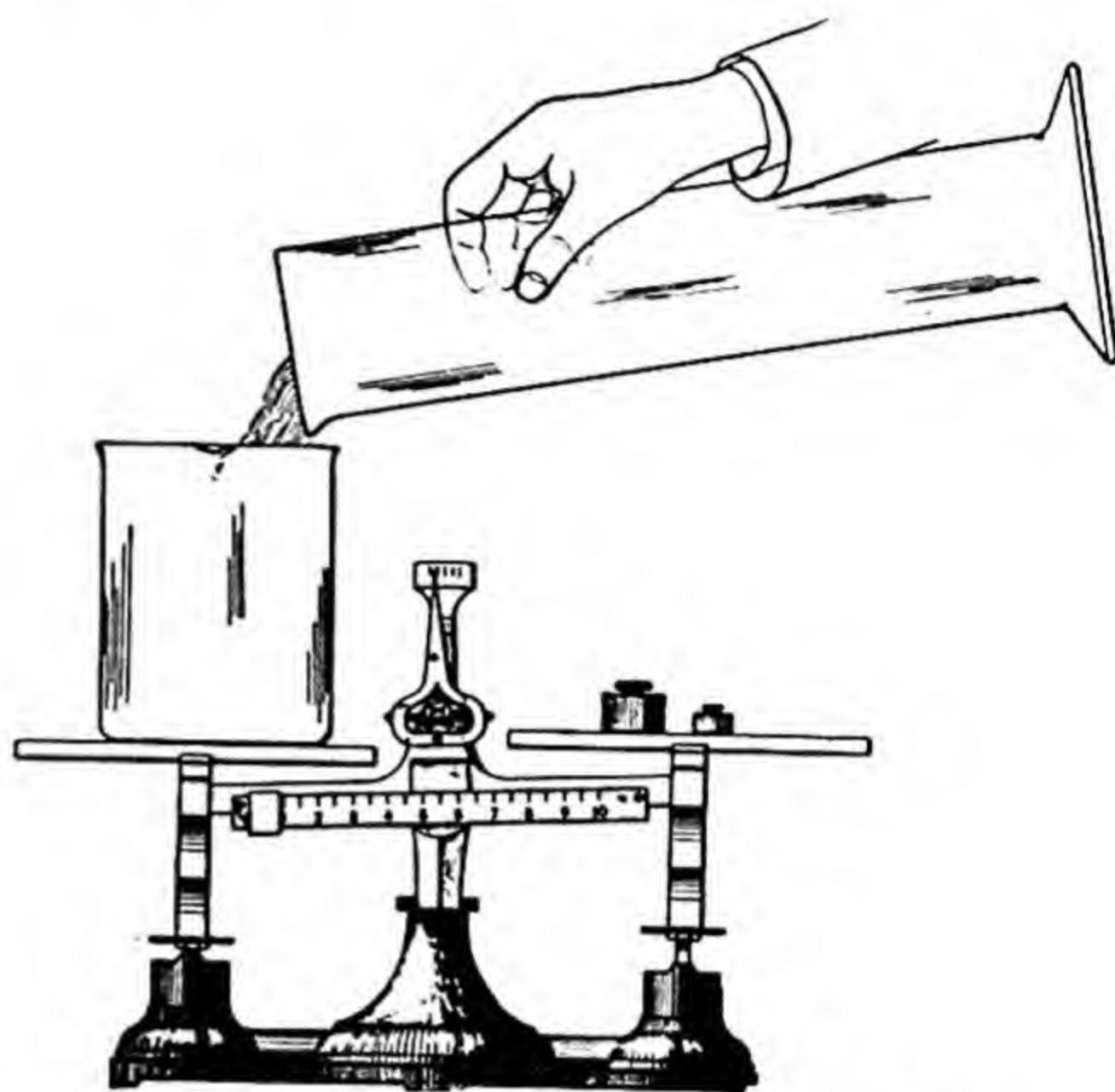


Fig. 137. Carbon dioxide is a heavy gas.

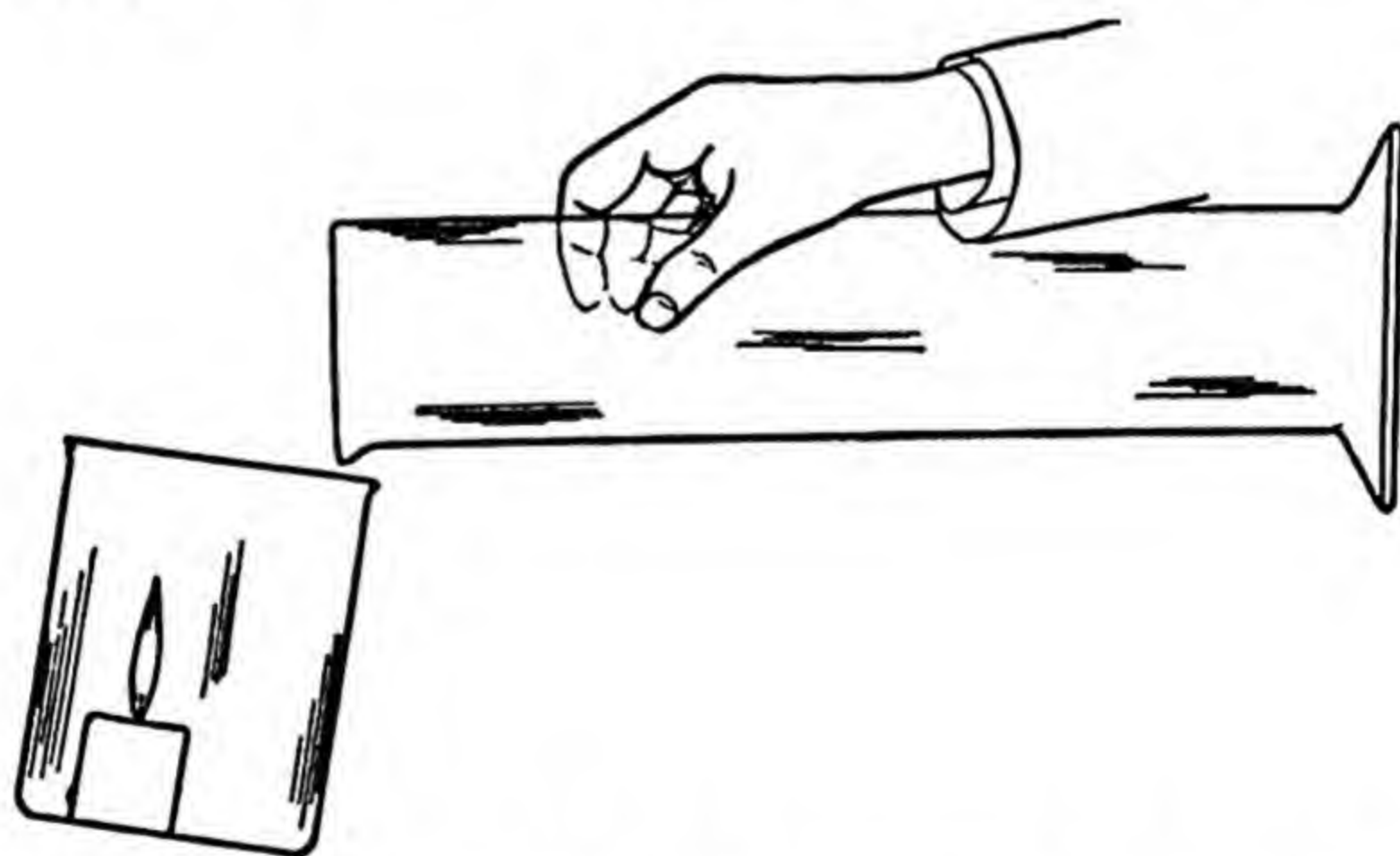


Fig. 138. Carbon dioxide can be poured from one vessel to another. It does not support the combustion of a candle.

displacement of air in a bottle arranged as shown in Fig. 136. Under standard conditions, 1 liter of carbon dioxide weighs 1.98 g. The same volume of air weighs 1.29 g. On account of this difference in density, carbon dioxide can be poured like water from one bottle to another.

Although we cannot see carbon dioxide gas, we can observe the effects of pouring it into a beaker in which a candle is burning. The gas extinguishes the flame as it fills the beaker. Mines and wells often become filled with carbon dioxide. A person descending into such a place may be suffocated because of lack of oxygen.

Carbon dioxide can be turned into a liquid by putting sufficient pressure on it. When it is allowed to evaporate again to a gas,



Courtesy, Walter Kidde Co.

Fig. 139. Rubber rafts have saved the lives of many army and navy aviators forced down at sea. To each raft is attached a steel cylinder filled with liquid carbon dioxide. A five-man raft (the larger one) requires 3.62 pounds of carbon dioxide to inflate it. The cylinder that contains this quantity of carbon dioxide is 22 inches long and about 3.7 inches in diameter, and weighs about 12 pounds.

it absorbs heat just as water does on evaporating, and everything in contact with the evaporating liquid becomes cold.

At 20°C . carbon dioxide can be liquefied by applying a pressure of 826 lb. per square inch. A pound of the liquid measures a little less than a pint. When the liquid evaporates at ordinary temperatures and under atmospheric pressure it expands to a volume more than 500 times the volume it occupies as a liquid.

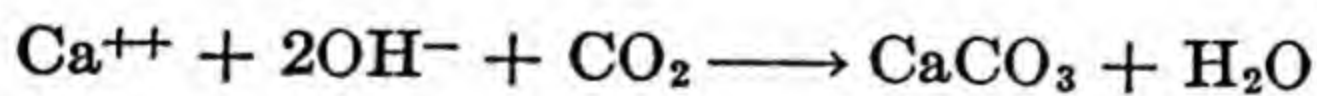
Ships in our Navy and airplanes which are designed to fly over water are equipped with collapsed rubber boats having carbon dioxide flasks and valves attached. Within a few seconds after the valve is opened a boat of this kind is inflated and ready to carry

its load. Many lives have been saved since these light, collapsible boats were invented. Eddie Rickenbacker and his companions rode on the Pacific Ocean in one of these boats for twenty-eight days after their airplane failed. Some shipwrecked men of the Navy have been rescued after floating on rafts for nearly three months. Less than four pounds of carbon dioxide suffice to inflate a five-man raft, and four pounds of the liquid can be carried in a steel cylinder four inches in diameter and only twenty inches long.

Dry ice. When liquid carbon dioxide is cooled by liquid air, or by any process which lowers the temperature to about $-60^{\circ}\text{C}.$, it freezes to a white solid. This solid carbon dioxide is called "dry ice" because it turns directly to a gas in the air without going through the liquid state. It is used extensively in refrigerator cars for transporting fruit, vegetables, and other kinds of foods. Ice cream may be carried long distances when packed in dry ice.

Some people carry dry ice in their automobiles when driving over a hot desert or through some of our interior valleys during the summer months. Care must be taken to have good ventilation in the car when this is done; otherwise there is danger of suffocation because of the large amount of carbon dioxide gas formed. Carbon dioxide is not a poisonous gas. It may cause a headache or even prove fatal if there is too much of it in the air we breathe, but the evil effect is due merely to a lack of oxygen. The more carbon dioxide there is in the air, the less oxygen we get in each breath. Carbon monoxide, on the other hand, is a very poisonous gas.

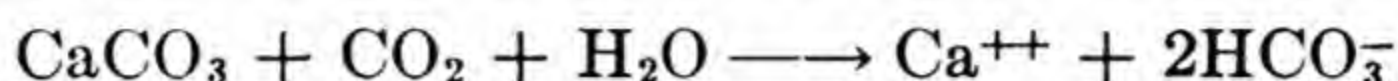
Test for carbon dioxide. Blow your breath through a glass tube into a clear solution of limewater. Filter the limewater before using it if it is not perfectly clear. The white precipitate formed is calcium carbonate.



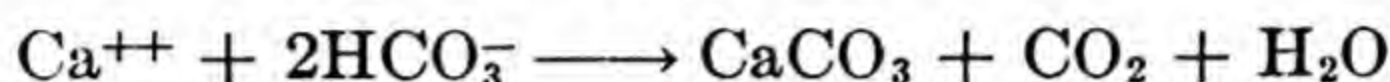
Add to the turbid mixture a few drops of hydrochloric acid. Does the precipitate dissolve? Is carbon dioxide evolved? What compound of calcium remains in the solution?

Chemical properties of carbon dioxide. Carbon dioxide does not burn, nor does it support the combustion of wood, coal, or other common fuels. A burning splinter thrust into a bottle of carbon dioxide is immediately extinguished. Some other substances will burn in an atmosphere of carbon dioxide; magnesium burns rapidly, forming magnesium oxide and carbon.

When carbon dioxide is led into a solution of limewater for some time, the precipitate at first formed slowly redissolves, leaving a clear solution. Calcium carbonate, with an excess of carbon dioxide, forms calcium bicarbonate, which is a soluble salt.



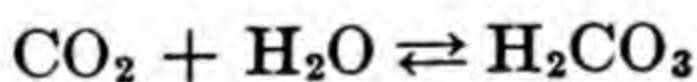
If the solution containing calcium ions and bicarbonate ions is heated to the boiling point, carbon dioxide passes off and calcium carbonate is again precipitated:



This equation is the reverse of the one for the formation of calcium bicarbonate from calcium carbonate. Dry calcium bicarbonate decomposes in the same way when heated:

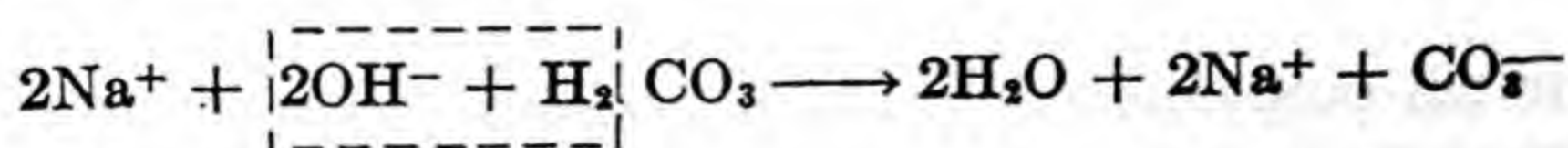


Carbonic acid. Carbon dioxide dissolves in water, forming a weak acid called *carbonic acid*. We have learned that the sour taste of the solution of an acid is due to the presence of hydrogen ions. Since soda water is almost tasteless and not noticeably sour, we must conclude that carbonic acid is an *extremely weak acid*. We therefore write its formula as H_2CO_3 rather than in the form of its ions, as is the custom with strong acids. The equation for the formation of carbonic acid by the solution of its anhydride, CO_2 , in water is written



If greater pressure is placed upon the gas, or if the water is cooled, more gas dissolves in the water, but it escapes when the pressure is reduced or when the solution is warmed. We represent the reversibility of the reaction by means of arrows pointing in both directions.

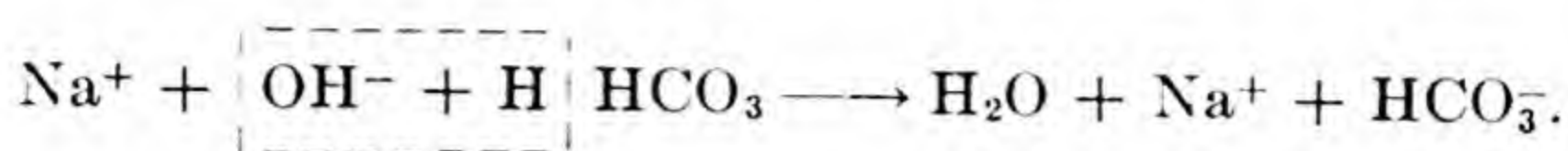
Carbonic acid reacts with bases, forming water and the corresponding salt. When both hydrogen atoms of the H_2CO_3 are neutralized, the normal carbonate is formed. For example, when carbonic acid is neutralized with sodium hydroxide, the products are water and sodium carbonate:



Since sodium carbonate is a soluble salt, it exists in the form of ions in the solution.

When only one of the hydrogen atoms in the carbonic acid molecule is neutralized, sodium hydrogen carbonate (usually

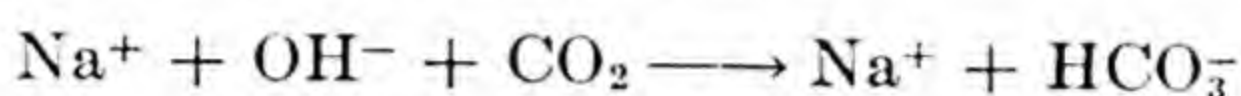
called sodium bicarbonate) is the salt formed:



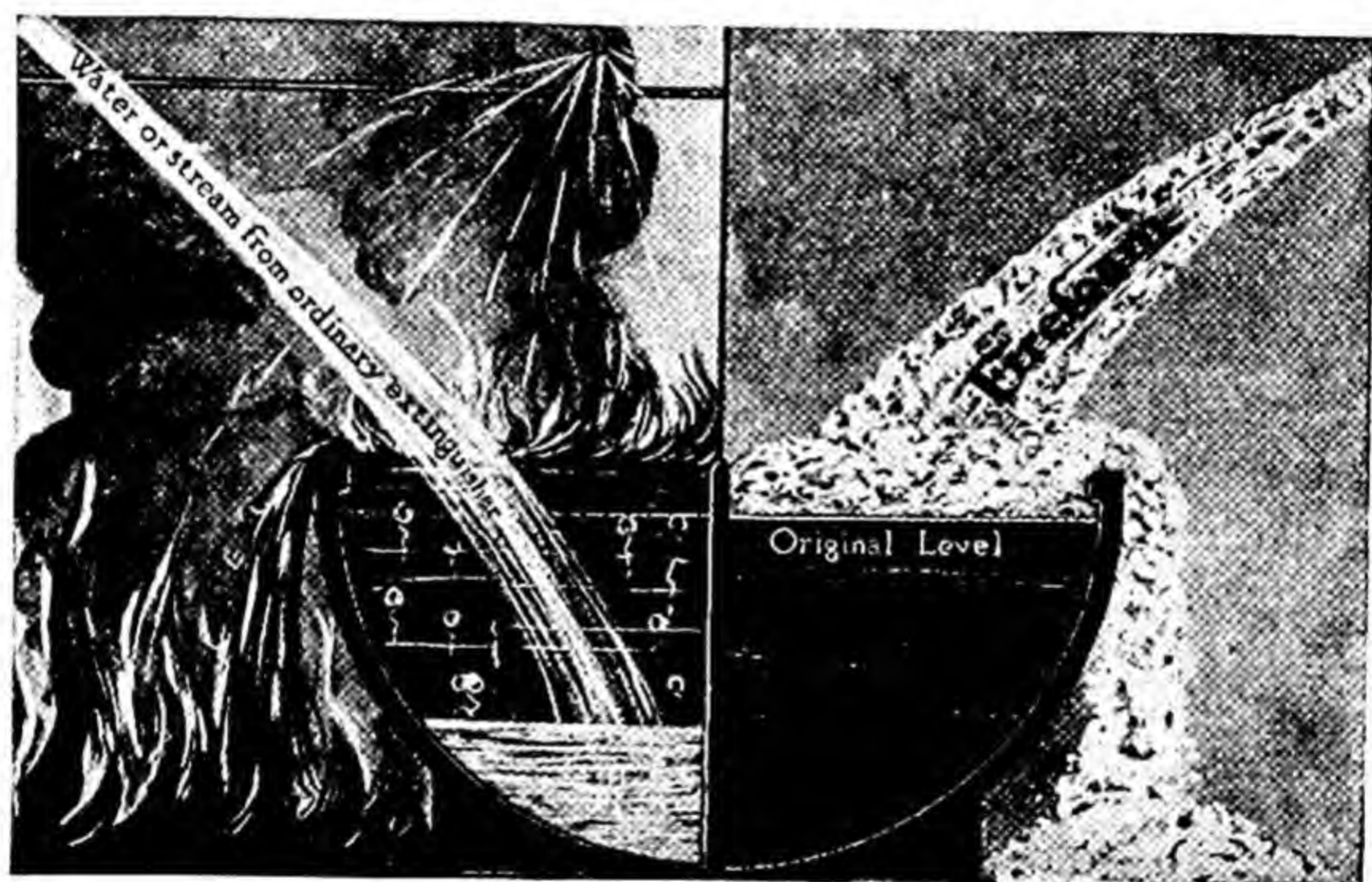
Carbon dioxide, the anhydride of carbonic acid, reacts in the same way:



With half as much base, the reaction is



Fire extinguishers. Carbon dioxide is often used to extinguish fires. It does not support combustion, and if a considerable

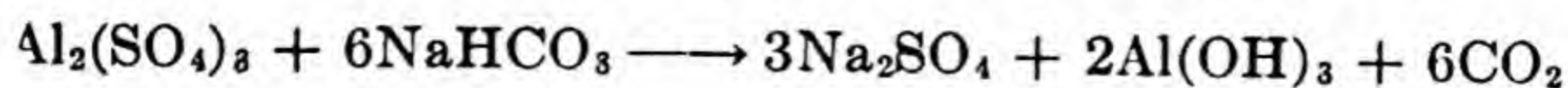


Courtesy, American-LaFrance-Foamite Co.

Fig. 140. Firefoam floats on the surface of burning oil and cuts off the supply of oxygen needed for combustion.

portion of the air surrounding a burning substance is replaced by carbon dioxide, the fire is extinguished. The best example of a method of replacing air by an atmosphere of carbon dioxide is found in the Foamite process. This process is used to extinguish fires in oil tanks. In the vicinity of oil-refining plants, petroleum is stored in enormous tanks, and occasionally the oil is ignited by a flash of lightning or by the careless use of a match.

Foamite. Carbon dioxide is generated by mixing solutions of sodium bicarbonate and aluminum sulfate. The solutions are conveyed in separate pipes to the oil tanks, where they are forced out through the same orifice onto the surface of the oil.



A substance called Foamite, obtained from licorice roots, is placed in the sodium bicarbonate solution. When this mixture comes in contact with aluminum hydroxide, $\text{Al}(\text{OH})_3$, it produces a viscous substance which forms a film around each bubble of carbon dioxide. The gas is held on the surface of the oil in the form of a heavy foam. The oil is thus effectively protected from the air by a blanket of carbon dioxide.



Courtesy, Fisher Scientific Co.

Fig. 141.
Phomene fire extinguisher.

A portable fire extinguisher. One type of portable fire extinguisher is shown in Fig. 141. It consists of a metal tank containing a solution of sodium bicarbonate and a bottle containing sulfuric acid. When the two components are mixed, carbon dioxide is released, and the pressure generated by the gas expels the liquid through a hose. The main purpose of the device is to force water onto the fire, but the liquid expelled is a little more effective than pure water would be, for it is saturated with carbon dioxide. The carbon dioxide gas entering the atmosphere and the water cooling the burning substance make an effective combination.

Liquid carbon dioxide is used in some portable fire extinguishers. The liquid is sprayed upon the burning material, and



Courtesy, Walter Kidde Co.

Fig. 142. Not smoke but a fog of carbon dioxide. Airplanes are equipped with tanks of liquid carbon dioxide for use in case of fire.

the fire is soon under control. The liquid provides very effective cooling and an inert atmosphere, and it does no damage to the

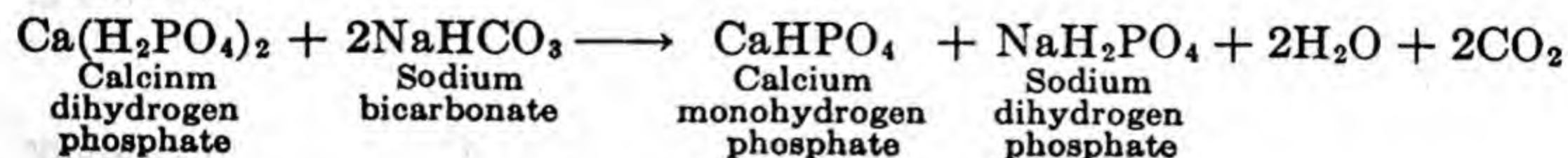
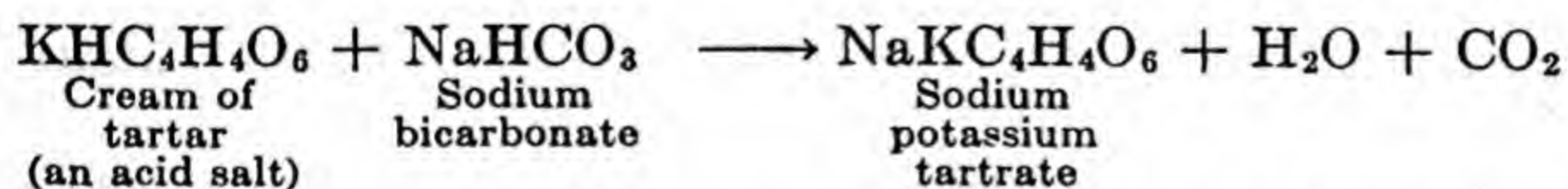
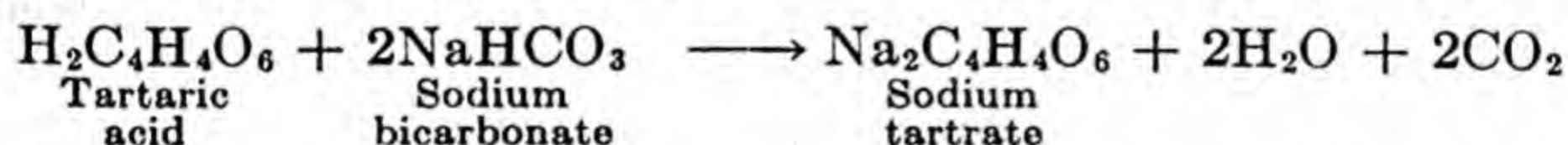
rescued property. Water used in fighting a fire is sometimes as destructive as the fire itself, especially in laboratories where fine electrical instruments are in use. The instruments are easily ruined by water. They are not damaged by liquid carbon dioxide.

Leavening. Carbon dioxide finds extensive use in the raising of bread and other kinds of bakery products. The leavening of bread is accomplished by the formation of carbon dioxide in the dough. The gas is produced in the dough by the action of yeast on sugar. The flour, when wet, forms a sticky substance that tends to prevent the escape of the carbon dioxide. The expansion of the gas within the mixture causes the whole mass to become light and porous. There is a further expansion or lightening of the loaf after it is placed in the oven, for the gas within the dough expands when heated. The dough is cooked in this expanded condition.

In the making of cake, baking powder is used. There are several kinds of baking powder, but they all contain sodium bicarbonate (baking soda) and some compound capable of forming hydrogen ions. One type of baking powder contains sodium bicarbonate and tartaric acid. No reaction occurs while the mixture is kept dry, but as soon as the powder is placed in water, the components ionize. Hydrogen ions come from the tartaric acid, and bicarbonate ions come from the soda. The following reaction then occurs:



The substances used in several kinds of baking powder are shown in the equations below. Do not try to memorize these equations, but notice that in each case carbon dioxide is liberated.



Questions and Exercises

1. Show how the two oxides of carbon illustrate the law of multiple proportions.
2. How many grams of carbon dioxide are formed when 200 g. of calcium carbonate are decomposed by heat?

3. Is carbon dioxide heavier or lighter than air?
4. Calculate the weight of 1 liter of carbon dioxide under standard conditions.
5. Determine the percentage of oxygen in carbon dioxide.
6. The molecular weight of magnesium carbonate is 84. Its composition is 28.57 per cent magnesium, 14.25 per cent carbon, and 57.14 per cent oxygen. Find its formula.
7. How would you proceed to determine whether a bottle contained carbon monoxide or carbon dioxide?
8. Describe three methods of obtaining carbon dioxide.
9. What is carbonic acid?
10. Write the equation for the reaction that takes place when carbon dioxide is bubbled through a solution of (a) calcium hydroxide; (b) potassium hydroxide.
11. Gas escapes from ginger ale when the container is first opened. How could you prove that the gas is carbon dioxide?
12. One ton of coal, when burned, yielded three tons of carbon dioxide. Calculate the per cent of carbon in the coal.
13. What weight of coke is required to reduce 10 tons of iron ore (Fe_2O_3) to iron? Assume that coke is 90 per cent carbon.
14. What weight of marble (CaCO_3) can be dissolved by 50 g. of sulfuric acid?
15. Assuming that each individual exhales 15 liters of carbon dioxide (measured at 0°C . and 1 atmosphere pressure) in an hour, calculate the weight and volume of carbon dioxide released in your classroom during one class period.
16. Devise a method of estimating the quantity of carbon dioxide in the atmosphere of the classroom.
17. Calculate the weight of carbon dioxide that would be released from 1 oz. of baking powder. Assume that the powder is composed of cream of tartar and sodium bicarbonate in the proportions indicated in the equation on page 305. What volume would the gas occupy at 0°C . and 760 mm.?
18. What volume of carbon dioxide is formed by burning 10 liters of carbon monoxide?
19. Is carbon monoxide heavier or lighter than air?
20. Calculate the weight of 1 liter of carbon monoxide at 0°C . and 1 atmosphere of pressure.
21. (a) How many grams of carbon monoxide can be prepared from 460 g. of formic acid? (b) How many liters of carbon monoxide, under standard conditions, does this represent?
22. Write an equation for the burning of methane (CH_4) in a limited supply of oxygen.
23. Determine the percentage composition of carbon monoxide.
24. What volume is occupied by 1 mole of carbon monoxide under standard conditions?
25. How many grams of oxalic acid would be required to liberate 44.8 liters of carbon monoxide under standard conditions?

26. What volume of oxygen will be required to burn 5 liters of carbon monoxide? What volume of carbon dioxide will be formed in this process?
27. Why should an automobile engine never be allowed to run in a closed garage?
28. Many automobile accidents which are caused on the highway in winter are due to carbon monoxide poisoning. Explain.
29. Why is forced ventilation provided in long automobile tunnels?
30. What is the use of sulfuric acid in the preparation of carbon monoxide from formic acid?
31. If you were given two bottles, one containing hydrogen and the other carbon monoxide, how would you distinguish between them?
32. Name two properties of carbon monoxide that make it useful.
33. How is carbon monoxide formed in a furnace?
34. Is it safe to sleep in a closed room in which a gas heater is burning?

PART 3

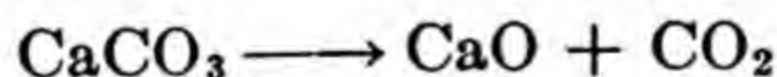
Salts of Carbonic Acid

Occurrence of carbonates and bicarbonates. The salts of carbonic acid, the carbonates and bicarbonates, are of great importance in many of our industries. There is a limited supply of these compounds in nature. The ashes of land plants contain potassium carbonate, while those of sea plants contain both sodium and potassium carbonates. These soluble salts are often extracted from the ash with water.

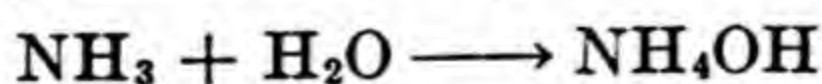
Solvay, a Belgian chemist, devised a method for making sodium bicarbonate cheaply on a large scale. Practically all the sodium carbonate used in the United States today is made by his method. The process enables us to make either sodium bicarbonate (baking soda) or the normal sodium carbonate (washing soda).

Sodium carbonate, Na_2CO_3 , is often called *soda ash*. When the compound is crystalline, it contains water of crystallization. Its formula is $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. This variety is known as *washing soda*, or *sal soda*.

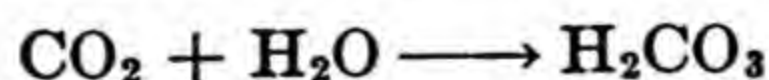
The Solvay process. The Solvay process is not difficult to understand. The raw materials used are limestone, sodium chloride, ammonia, and water. Limestone, CaCO_3 , is heated to a high temperature to decompose it into calcium oxide, CaO , and carbon dioxide, CO_2 :



Carbon dioxide and ammonia are added to water, and a solution of ammonium bicarbonate results. The ammonia gas dissolves in the water, forming ammonium hydroxide, a base:



Carbonic acid is formed when carbon dioxide dissolves in water:



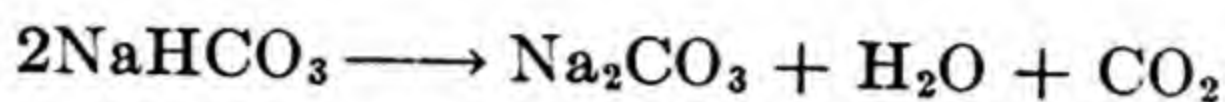
The ammonium hydroxide then neutralizes the carbonic acid, forming water and ammonium bicarbonate, a soluble salt which remains in solution:



The ammonium bicarbonate solution is then mixed with a solution of sodium chloride. Sodium bicarbonate precipitates from the mixture, for it is not very soluble in water containing an excess of sodium chloride:

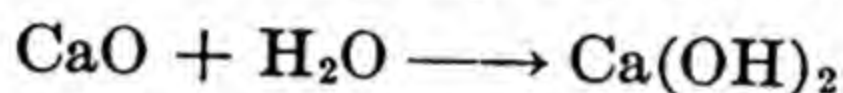


The sodium bicarbonate is filtered from the solution and heated. Carbon dioxide and water are given off, and sodium carbonate remains:

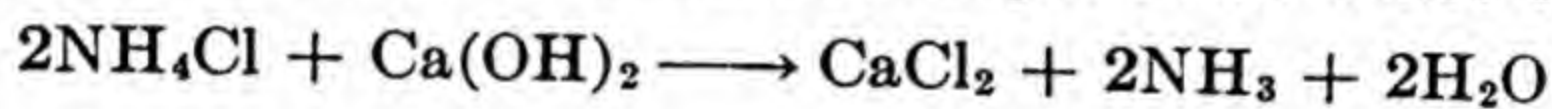


If sodium bicarbonate is the product desired, the final step in the process is omitted.

Ammonia is the most expensive substance used in the process. It is recovered from the ammonium chloride solution by treating the solution with the lime, CaO . You will remember that lime (calcium oxide) is the by-product obtained when carbon dioxide is formed from limestone. The calcium oxide is converted into calcium hydroxide (slaked lime) by treatment with water:

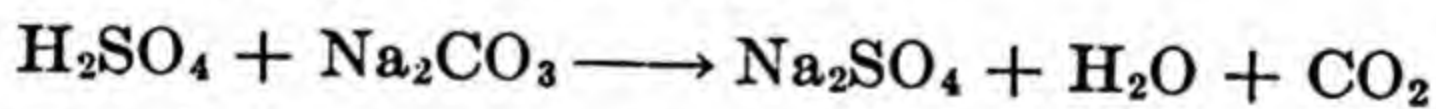


Ammonium chloride and calcium hydroxide react as follows:



The ammonia released in this reaction is again used to make more ammonium bicarbonate.

Uses of the carbonates and bicarbonates. Sodium carbonate is used in large quantities in the manufacture of glass. Large amounts are used also in the softening of water and in the preparation of soap powders. It is used to neutralize the sulfuric acid employed in refining petroleum oils:

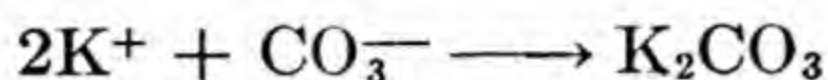


Sodium bicarbonate is used in all baking powders. It is often used as a medicine to neutralize an excess of acid in the stomach.

Potassium carbonate. Potassium carbonate, K_2CO_3 , cannot be made by a method like the Solvay process, for potassium bicarbonate does not precipitate when ammonium bicarbonate is added to a solution of potassium chloride. Potassium bicarbonate is soluble in such a solution.

Potassium carbonate is made from a solution of sodium carbonate and potassium chloride. When these salts are added to water, the ions Na^+ , K^+ , Cl^- , and CO_3^{--} are produced. These ions can combine to form the salts NaCl , KCl , Na_2CO_3 , and K_2CO_3 .

Nearly all salts are more soluble in hot water than in cold water, but the change in solubility corresponding to a certain change in temperature is not the same for all salts. If a hot solution containing the ions Na^+ , K^+ , Cl^- , and CO_3^{--} is cooled, the first salt to precipitate is potassium carbonate, for the solubility of potassium carbonate is reduced rapidly by cooling. The reaction which takes place when this occurs is



The Na^+ and Cl^- ions remain in the solution. Small amounts of K^+ and CO_3^{--} ions are left in the solution also because potassium carbonate is not absolutely insoluble. In the manufacturing process, hot solutions of sodium carbonate and potassium chloride are mixed and then allowed to cool until potassium carbonate precipitates:



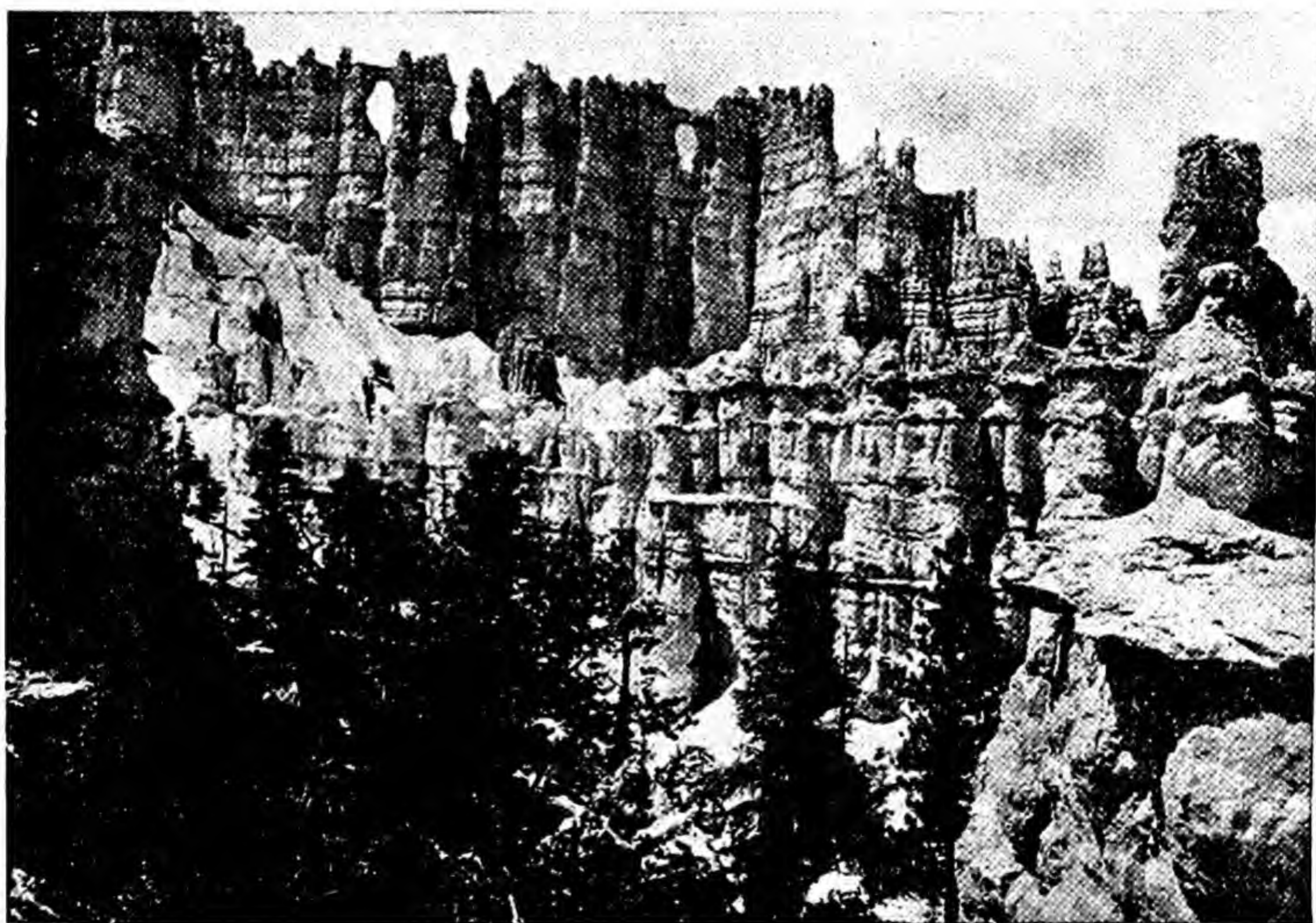
Questions and Exercises

1. Write equations representing the Solvay process for making sodium carbonate.
2. Write the equation for the reaction which takes place in a carbonate fire extinguisher.
3. What volume of ammonia can be produced by treating 1 kg. (kilogram) of ammonium chloride with slaked lime?
4. How could you make sodium bicarbonate from sodium carbonate?
5. What is the percentage composition of sal soda?
6. Name three uses of sodium carbonate.
7. Name two uses of sodium bicarbonate.
8. What is the formula for (a) washing soda; (b) baking soda?
9. How much sodium carbonate could be obtained by the Solvay process from 2 kg. of sodium chloride?
10. How many liters of carbon dioxide, measured under standard conditions, would be required to make 1060 g. of sodium carbonate?

PART 4

Silicon and Its Compounds

Silicon is the second element in Group IV of the Periodic Table. Since it has four valence electrons, as has carbon, we should expect it to form compounds similar to those of carbon. In many ways the compounds of silicon resemble those of carbon.



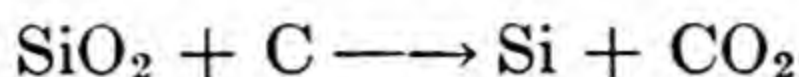
Courtesy, Union Pacific System

Fig. 143. Bryce Canyon, Utah. Mountains of limestone and silica have been carved into fantastic forms by wind and rain.

Occurrence. Silicon is never found in the free state, although next to oxygen it is the most abundant of the elements. With the exception of limestone and other carbonates, nearly all the rocks on the surface of the earth are compounds of silicon.

Preparation. Free silicon may be obtained from sand or crushed quartz by heating it with coke. Sand and quartz are

composed of silicon dioxide, SiO_2 , which is commonly called silica. When a mixture of coke and silica is heated in an electric furnace, carbon dioxide escapes and silicon remains as a nonvolatile residue:



The silicon made in this way is often impure.

Silicon may be obtained in a pure state by heating silica with magnesium powder:



The magnesium oxide and excess of free magnesium are removed by treatment with dilute hydrochloric acid.

Properties and uses of silicon. The principal physical properties of silicon are given in the table below.

PHYSICAL PROPERTIES OF SILICON

Atomic number.....	14	Electrons in shells:	
Atomic weight.....	28.06	1st shell.....	2
Isotopes.....	28, 29, 30	2nd shell.....	8
Density.....	2.4	3rd shell.....	4
Melting point, °C.....	1427		
Boiling point, °C.....	2287		

Silicon occurs in both crystalline and amorphous forms. The crystals are shiny, steel-blue, brittle needles. The amorphous form is a brown powder.

When silicon burns, it forms the dioxide SiO_2 . At red heat silicon acts upon water, liberating hydrogen and forming silicon dioxide. Iron containing silicon is used in the manufacture of acidproof castings, pipes, and laboratory apparatus. Duriron, an alloy consisting of 86 per cent iron and 14 per cent silicon, is used extensively for drain pipes in chemical laboratories.

Carborundum. If an excess of carbon is mixed with sand in the electric furnace, silicon carbide, SiC , commonly called carborundum, is formed:

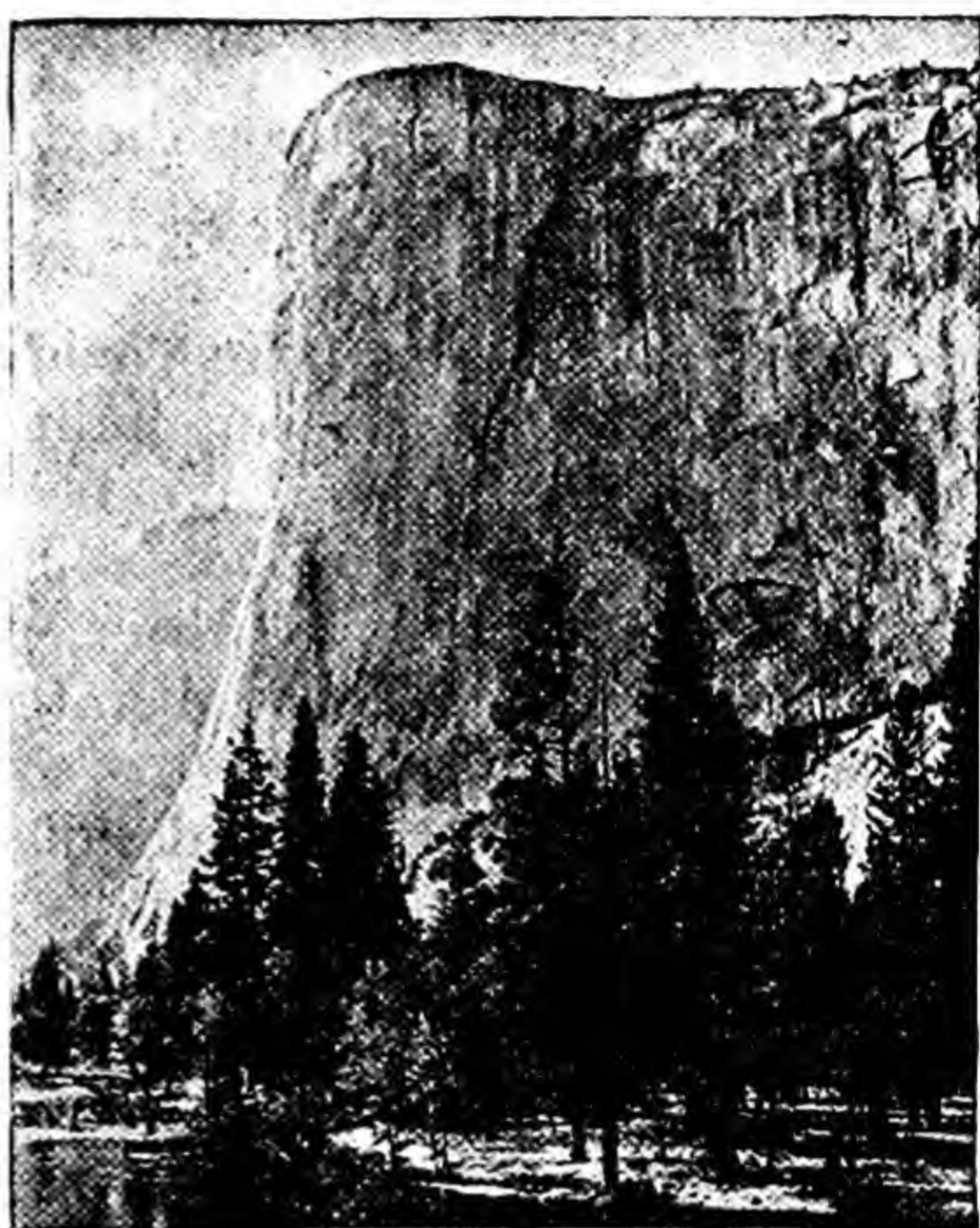


With the single exception of diamond, carborundum is the hardest substance known. It is ground into fine particles which are cemented together to form whetstones and other types of grinding surfaces.

Silicon monoxide. Silicon monoxide, corresponding to carbon monoxide, has been formed, but is of slight importance.

Silicon dioxide. The sands of the seashore and of the deserts are composed principally of silicon dioxide. Vast mountains of

sandstone have the same composition. Granite is composed of quartz, feldspar, and mica. Feldspar and mica contain silicon dioxide in combination with metallic oxides. Quartz is a pure crystalline form of silicon dioxide. Many beautiful stones consist of quartz combined with small quantities of other substances which impart characteristic colors to the crystals. Onyx, agate, flint, opal, jasper, and amethyst are forms of silica, with varying quantities of water and small amounts of metallic oxides. The purple color of amethyst is due to the presence of manganese. Sandstone and quartzite (quartz combined with various basic oxides) are used extensively as building stones.



Courtesy, National Parks Service

Fig. 144. A mountain of granite. El Capitan, Yosemite National Park.

Sand is "weathered" quartz, broken into small, hard particles.



Courtesy, National Parks Service

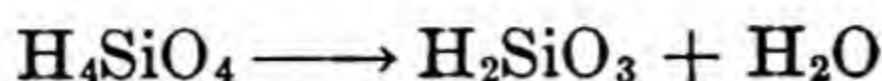
Fig. 145. A petrified tree resting on sandstone pillars.

Sandpaper is made by attaching sand to paper by means of glue. It is used for smoothing the surface of wood and metals. Sand driven by compressed air (a sand blast) is often used for cleaning metal surfaces or the walls of stucco buildings. Sand is used also in enormous quantities in the manufacture of glass, porcelain, and mortar.

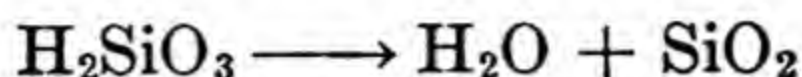
Acids of silicon. Silicon dioxide is the anhydride of the silicic acids, H_4SiO_4 and H_2SiO_3 . Their formulas differ by one molecule of water. There are several acidic substances composed of silicon dioxide and water in other proportions.

When orthosilicic acid, H_4SiO_4 , is heated, it loses water and

becomes *metasilicic acid*, H_2SiO_3 :

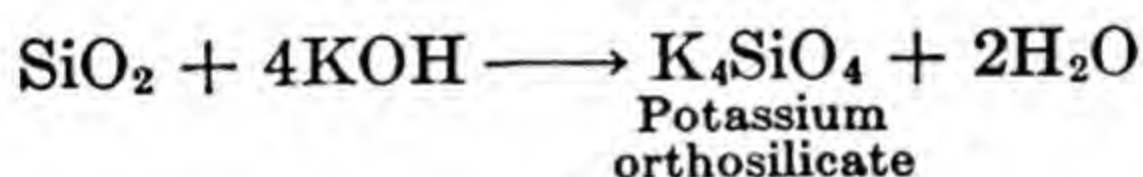
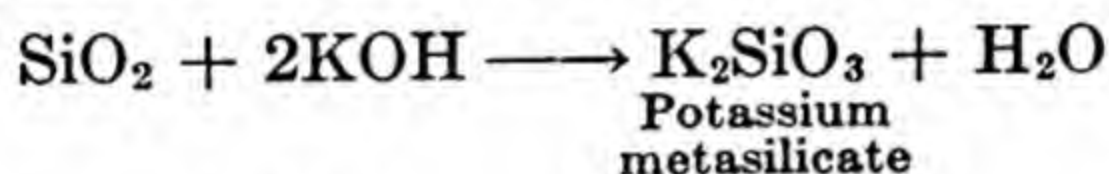


On further heating, silicon dioxide is formed:



There are traces of silicic acid in ground water in many regions. Cones of silica have been built up around the craters of some geysers. Buried trees have been petrified by the deposition of silica in the decaying wood. Silicic acid and its salts the silicates, dissolved in the ground water, permeate the buried tree, and as the woody material slowly disintegrates and dissolves, it is replaced by silica. The process occurs so gradually that the original form of the tree is preserved in detail.

Silicates. Silicon dioxide is not soluble in water, but it dissolves in molten alkalies, forming salts of silicic acids. By acidifying the solution of their salts, the silicic acids are obtained.



Although the silicic acids decompose easily into water and silicon dioxide, the salts of these acids are very stable compounds. Calcium silicate, CaSiO_3 ; magnesium silicate, MgSiO_3 ; and aluminum silicate, $\text{Al}_2(\text{SiO}_3)_3$, are components of rocks, soils, and clays in all parts of the world.

Asbestos is composed of magnesium silicate mixed with varying quantities of silicates of calcium and iron. It is a fibrous, non-combustible mineral and is used in the manufacture of fireproof curtains and shingles.

Soluble silicates, such as Na_2SiO_3 and Na_4SiO_4 , can be made by fusing fine sand with sodium carbonate. Carbon dioxide is evolved in the process. These silicates are the main components of water glass, which is used as an adhesive and as a filler in some kinds of soap, and as a preservative for eggs. The pores in the shells of the eggs become coated and sealed with the gelatinous silicate, and air cannot get through the shell. Decomposition is retarded by excluding the air.

Glass. Ordinary glass is made by melting a mixture of sand, sodium carbonate, and calcium carbonate. Other components are used in the preparation of special kinds of glass. For the production of clear, colorless, transparent glass, it is necessary to

use sand which is nearly pure silicon dioxide. The common impurities in sand are oxides of iron and aluminum. Iron produces a green or yellowish-green color in the glass. The color is not objectionable in bottles, but is very undesirable in windows.

Typical batches of materials to be fused for the production of glass are shown below.

LIME GLASS		LEAD GLASS	
<i>Components</i>	<i>Parts by Weight</i>	<i>Components</i>	<i>Parts by Weight</i>
Sand.....	100	Sand.....	100
Sodium carbonate.....	30	Potassium carbonate.....	35
Calcium carbonate.....	30	Red lead, Pb_3O_4	60
		Sodium nitrate.....	10

Glass is a mixture of silicates and not a definite chemical compound. It has no definite melting point, but softens gradually when heated. The silicates of most metals are difficult to fuse, and they crystallize when the molten material cools. Alkali silicates fuse easily, and the molten mass remains amorphous after cooling. Glass is a solution of one silicate in another, and it remains plastic over a large range of temperatures. This makes it possible to draw, mold, or blow the material into any desired shape while it is cooling. Lime glass is used for windows, bottles, and common glassware. Lead glass is heavy and has a brilliant luster. It is used for cut glassware and for lenses and prisms in optical instruments.

Plate glass is made by pouring the molten silicate mixture on a large iron plate. It flows over the smooth iron surface, forming an even layer. To insure uniform thickness, it is rolled with heavy, hot iron rollers which travel on adjustable guides at the edges of the iron plate or casting table. After it has been rolled, the glass is placed in an annealing furnace, where it is cooled very slowly. Glass that has been cooled quickly is brittle and breaks easily. Slow cooling (annealing) gives the molecules a chance to arrange themselves in the plastic mass in such a way as to avoid internal strain. The surface of the glass is made perfectly smooth by grinding it first with iron rubbers and sand, then with leather-covered rubbers and fine emery dust. In many cases of grinding and polishing, the finished product is not much more than half as thick as the original plate.

Window glass is made by rolling the plastic material into thin sheets. In some factories window glass is made by blowing the molten glass with a blowpipe which is connected with a tank of compressed air. The pipe is withdrawn slowly while a carefully regulated flow of air is maintained. By this means the glass is

blown into a cylinder several feet long. The cylinder is then detached from the blowpipe and cut lengthwise with a diamond cutter. It is placed on a flat surface in a furnace, with the cut side up, and heated until it softens and the cylinder slowly opens and flattens out. It is then annealed and finally cut into sheets of desired sizes.

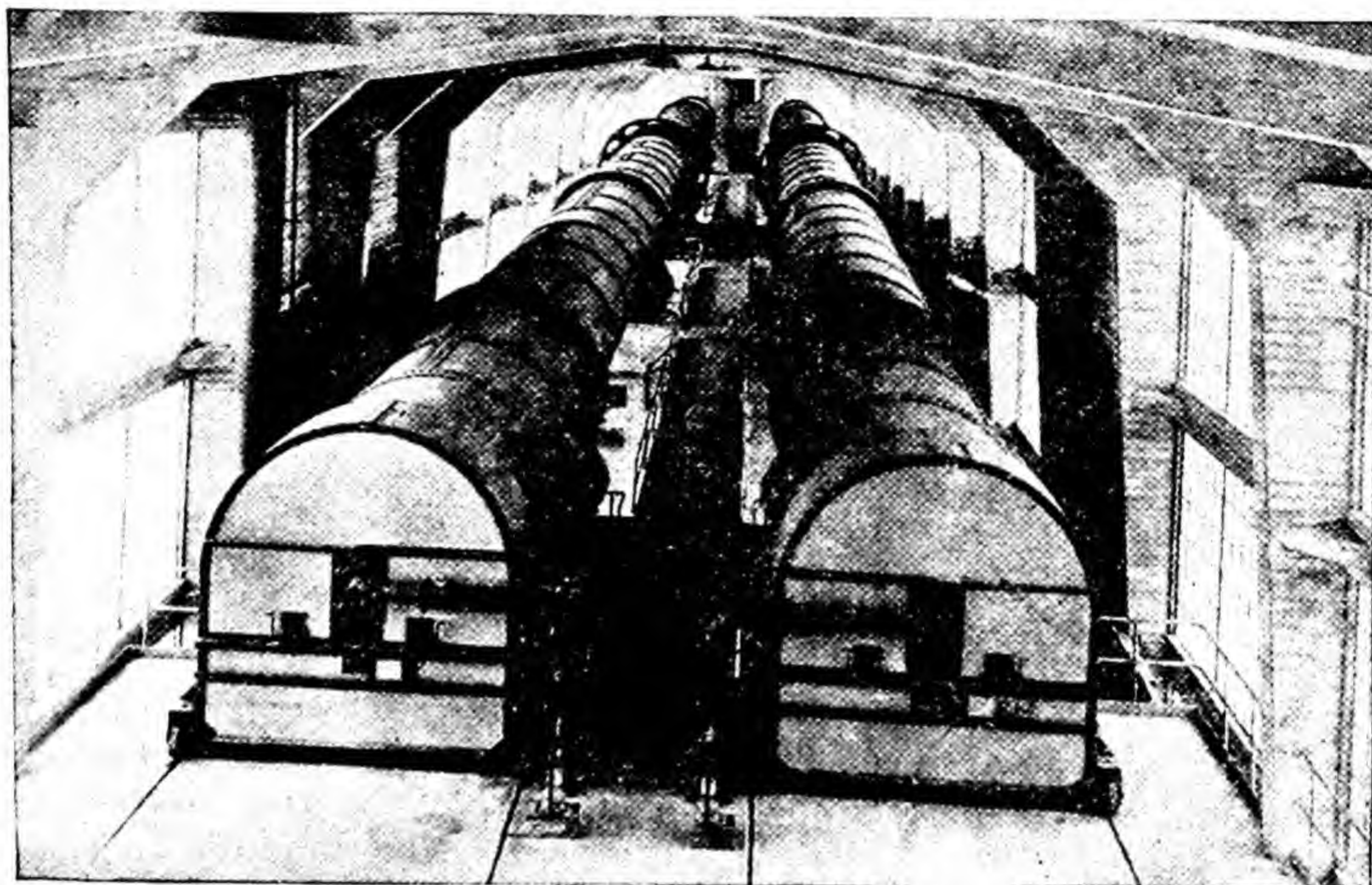
Glass made from pure molten quartz can be heated to a very high temperature without melting. This property makes silica glass valuable in the construction of transparent parts of apparatus that must be subjected to high temperatures. Ordinary glass softens at temperatures between 500° and 900°C . Hot quartz glass can be plunged into cold water without danger of breaking it. Windows made from fused quartz look like ordinary glass, but they are transparent to ultraviolet light as well as to visible light. Ultraviolet light does not pass through ordinary glass. On that account quartz is used in the construction of many optical instruments and in the manufacture of arc lamps that are designed to produce ultraviolet rays.

Pyrex glass is now in general use in chemical laboratories, and it is employed quite extensively in the home. It can be heated and cooled rapidly with little danger of breaking. Pyrex glass contains boron and aluminum and a large excess of silica. It is made by fusing together aluminum oxide, Al_2O_3 ; borax, $\text{Na}_2\text{B}_4\text{O}_7$; and white sand, SiO_2 .

Porcelain. Ordinary clay is aluminum silicate mixed with varying quantities of calcium carbonate, magnesium carbonate, feldspar, silica, and iron compounds. Such clays are used in making bricks, tiles, drainpipes, and flowerpots. Kaolin is a clay that is practically pure hydrated aluminum silicate; that is, aluminum silicate combined with a definite quantity of water. It corresponds approximately to the formula $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$. It is used in the manufacture of porcelain or chinaware. Kaolin, fine white sand, and powdered feldspar are mixed with enough water to make a plastic mass, and the material is pressed into molds. These objects are then heated almost to the point of fusion. After cooling, they are dipped in a suspension of glazing material which is composed of fusible silicates and salts. The pieces are then returned to the kiln and fired again, the fusible layer melting and filling the pores of the clay, producing a smooth, impervious surface. Cups, saucers, and plates are made in this way.

Cement. Silicates of calcium and aluminum are used in the manufacture of cement. Cement readily combines with water, forming a hard mass composed chiefly of crystals of hydrous

silicates, and since water is used in the reaction that causes the setting or hardening, cement structures can be built under water as well as on the land. Portland cement is made by heating a mixture of clay and finely powdered limestone until the mass begins to melt. This heating is accomplished by passing the powdered mixture through a long, rotary kiln. The huge steel tube that constitutes the kiln may be from 70 to 200 ft. long and 6 or 8 ft. in diameter, and is lined with firebrick. It is slightly inclined, mounted on roller bearings, and geared to a rotating



Courtesy, Allis-Chalmers Mfg. Co.

Fig. 146. Rotary kilns used in the manufacture of cement.

shaft. The powdered material is fed into the elevated end of the kiln, and as the kiln turns, the material gradually moves toward the lower end, requiring two or three hours for passage through the tube.

The process is continuous; a steady supply of materials is fed into the upper end of the furnace, and the calcined product falls continuously from the lower end. The kiln is heated by burning powdered coal in an air blast. The coal is blown into the lower end of the kiln by compressed air, and a roaring flame, in contact with the powdered limestone and clay, heats the mixture to approximately 1500°C . The limestone is decomposed into carbon dioxide and calcium oxide, the carbon dioxide escapes, and the calcium oxide combines with the aluminum silicate as the

whole mass sinters (nearly fuses). The product emerges from the kiln as small, red-hot clumps, called *clinker*. The clinker is cooled and conveyed to grinding mills, where it is reduced to a fine powder. The finished product contains tricalcium silicate, Ca_3SiO_5 ; tricalcium aluminate, $\text{Ca}_3\text{Al}_2\text{O}_6$; and small quantities of other compounds.

This process for making cement was developed in England in 1824. In color and texture, the hardened product resembled the building stone quarried at Portland, England, and on that account the artificial stone was named Portland cement. Cements prepared at different plants are not exactly alike.

COMPOSITIONS PER CENT OF TWO TYPICAL COMMERCIAL PORTLAND CEMENTS

Component	I	II
SiO_2	21.10	21.69
Al_2O_3	9.00	6.56
Fe_2O_3	4.40	3.95
CaO	61.45	62.80
MgO	1.37	3.00
SO_3	1.28	1.50
Na_2O	0.68	—
K_2O and CO_2	0.72	0.50
	100.00	100.00

Mountains of limestone and of shale are found in the same vicinity in many parts of the world. From the two sources a mixture can be made that is suitable for the manufacture of cement. In some localities deposits of marl (chiefly calcium carbonate) and clay are found together on the floors of ancient lakes or inland seas, and these deposits are often so finely divided that no preliminary grinding is necessary. Such deposits are converted into cement at a very low cost. The marl and clay are placed in separate tanks, and enough water is added to each to make it possible to pump the mud from one storage tank to another. The two components are mixed in proper proportions, and this muddy mixture, called a *slurry*, is pumped directly into the upper end of the rotary kiln. The water is evaporated in the upper third of the kiln, and the clinker is formed in the lower two-thirds of the tube.

Concrete. Cement is mixed with gravel, sand, and water in the preparation of concrete. In the setting, water combines with the cement to form hydrated calcium silicates and aluminates. It is in this form that the major part of the world's supply of

cement is used. Reinforced concrete is made by embedding iron rods in ordinary concrete. Large buildings, bridges, tunnels, and

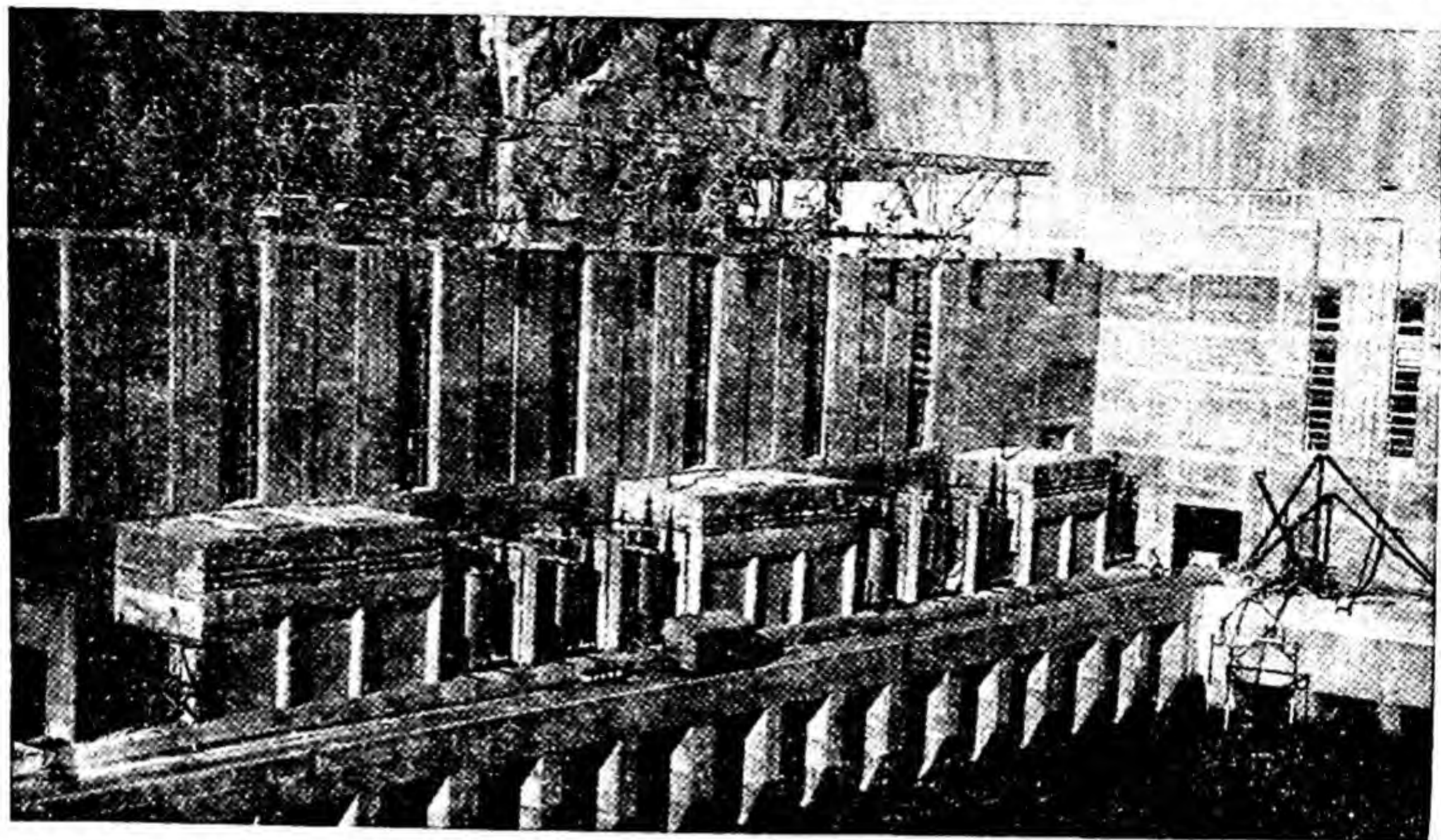


Fig. 147. A section of the power plant at Boulder Dam. The dam is one of the largest reinforced concrete structures in the world.

tubes are built of reinforced concrete, which is one of the most important building materials in the world today.

Questions and Exercises

1. Write an equation for the preparation of pure silicon.
2. What proportion of the earth's crust is silicon?
3. Name the commonest and most abundant compound of silicon.
4. What is duriron, and what property of the substance depends primarily upon its silicon content?
5. Of what elements is the mineral called *asbestos* composed?
6. How is ordinary glass made?
7. Is glass a single compound or a mixture of several compounds?
8. Compare the properties of ordinary lime glass and of glass made by fusing pure quartz alone.
9. What is porcelain? How is it made?
10. Why does cement set under water?
11. Molasses is a solution which if heated becomes more fluid, and if cooled sufficiently becomes viscous or hard. The hardening in this case takes place gradually, and no crystals separate out. We call such a solid a supercooled liquid. A solution of salt in water, on the other hand, when cooled precipitates either crystals of ice or salt and does not become solid in a gradual way. Is glass a crystalline substance or a supercooled liquid?

12. What weight of magnesium is required to reduce 30 g. of silicon dioxide to free silicon?
13. What is glass? Describe a process for making it.
14. What volume of carbon monoxide measured at standard conditions would be formed if 30 g. of sand were heated with enough coke to convert the mixture into carborundum?
15. What is Portland cement? How is it manufactured?
16. Write an equation showing how SiO_2 is formed from silicic acid.
17. What is the difference between pyrex glass and ordinary glass?
18. Make a table showing the resemblance between the compounds of carbon and those of silicon which you have studied.
19. Why would you expect the elements carbon and silicon to form similar compounds?
20. Name some common uses of carborundum.

PART 5

Titanium, Zirconium, Hafnium, and Thorium

The first two members of Group IV of the Periodic Table are nonmetals. Titanium, zirconium, hafnium, and thorium are metallic elements.

These elements are not nearly so rare as has been commonly supposed. They never occur free in nature, but their compounds are widely distributed. Titanium ranks eighth in order of abundance among the metals in igneous rocks.

The principal physical properties of these metals are shown in the following table.

	Ti	Zr	Hf	Th
Atomic number.....	22	40	72	90
Atomic weight.....	47.90	91.22	178.6	232.12
Isotopes.....	{ 46, 47, 48, 49, 50	90, 91, 92, 94, 96	176, 177, 178, 179, 180	—
Melting point, °C.....	1800	1700	1700	1845
Boiling point, °C.....	3000	2900	3200	3000
Density.....	4.5	6.4	11.4	11.2

Titanium

The most important titanium ores are ilmenite, FeTiO_3 , rutile, TiO_2 , and arizonite, $\text{Fe}_2\text{O}_3 \cdot 3\text{TiO}_2$. It is difficult to obtain the pure element titanium from its ores. A fairly pure product may be obtained by heating the chloride of the element with sodium in a steel bomb, or the oxide may be reduced by carbon or aluminum in an electric furnace, but in either case an impure product is obtained.

Titanium is usually described as being hard and brittle. It is a good conductor of electricity. There is no practical use at the present time for pure titanium, but an alloy of titanium and iron is used extensively in the steel industry. Titanium imparts toughness to steel, and renders the alloy capable of withstanding sudden shocks. At high temperatures titanium unites with nitrogen to form the solid nitride, TiN .

Titanium dioxide has become one of the most important white pigments. The sand of certain beaches in India is the principal commercial source of the dioxide. It is used also to impart a yellow color to glassware. Titanium chloride, TiCl_4 , hydrolyzes readily when it comes in contact with water, and when sprayed into the air from an airplane it forms a dense white smoke which may be used as a smoke screen. The smoke consists of fine particles of titanium oxide and hydroxide.

Zirconium

The most extensive ores of zirconium are the dioxide, ZrO_2 , and the silicate, zircon, having the formula ZrSiO_4 . Brazil is the source of most of the zirconium ores. The metal is separated from its compounds in a manner similar to that for obtaining titanium. It is obtained from the oxide by heating with aluminum powder, and it is separated from the mixture by distillation. An alloy with iron, ferrozirconium, has been used to some extent in the steel industry. The most important compound of zirconium is zirconia, ZrO_2 , which is used as a lining for furnaces. The naturally occurring silicate, zircon, is valued as a jewel. Because of their luster and hardness, zircons are often used as substitutes for diamonds. They are found in a variety of colors—red, green, blue, and white.

Hafnium

The element hafnium was unknown until 1923, although it is present to the extent of 1 or 2 per cent in practically all zirconium ores. Zirconium and hafnium form similar compounds with nearly the same melting points and boiling points. No wonder that its discovery was made so recently.

Thorium

Thorium occurs in nature in the form of the orthosilicate, ThSiO_4 . This is the black mineral called thorite. There is also an orange mineral of a similar composition called orangite. The principle source of commercial thorium is monazite sand, found in Brazil and India. The pure metal, which may be prepared by the reduction of the oxide by calcium in a steel bomb, has no practical uses. It is a radioactive element, similar to uranium.

When a mixture of the oxides of thorium and cerium are heated to a high temperature, they give out an intense white light. The Welsbach gas mantle contains these two oxides. The mantles are made by saturating fabrics with the nitrates of thorium and cerium, then subjecting the preparations to heat. The fabric burns out, and the nitrates are changed to oxides, which retain the shape of the original fabric.

UNIT X

Group VI of the Periodic Table: Sulfur, Selenium, and Tellurium

PART 1

Sulfur

The first member of Group VI of the Periodic Table, oxygen, has already been studied in some detail. The other important members of the group are sulfur, selenium, and tellurium. The principal physical constants of these elements are given in the following table.

	S	Se	Te
Atomic number.....	16	34	52
Atomic weight.....	32.06	78.96	127.61
Isotopes.....	32, 33, 34, 36	74, 76, 77, 78, 80, 82	120, 122, 123, 124, 125, 126, 128, 130
Electron structure:			
1st shell.....	2	2	2
2nd shell.....	8	8	8
3rd shell.....	6	18	18
4th shell.....	—	6	18
5th shell.....	—	—	6
Melting point, °C.....	114.5	217	450
Boiling point, °C.....	444.6	688	1390

Sulfur, the second member of Group VI in the Periodic Table, is one of the most familiar and useful of the elements. It was known to man in the earliest periods of recorded history. It is mentioned in the Old Testament and in other books of ancient origin.

Occurrence. Sulfur is found in nature in the free state and in combination with other elements. Free sulfur is found in every region where volcanic activity has taken place. The most important deposits are in Sicily and in Texas and Louisiana. About 80 per cent of the world's supply is obtained from these two

states in our own country. The sulfur occurs in huge masses under layers of sand and clay. It is estimated that more than 300,000 tons of sulfur are produced annually in the United States.

Sulfur is found combined with iron, copper, zinc, lead, and many other metals in the form of sulfides. Sulfates of some of the metals also are found, including magnesium sulfate, commonly called "Epsom salts," and barium sulfate, "barite."

Extraction. In Sicily the sulfur is contaminated with pumice and other kinds of volcanic rock. It is extracted from the rock by heating the mass and collecting the sulfur, which melts and runs out of the

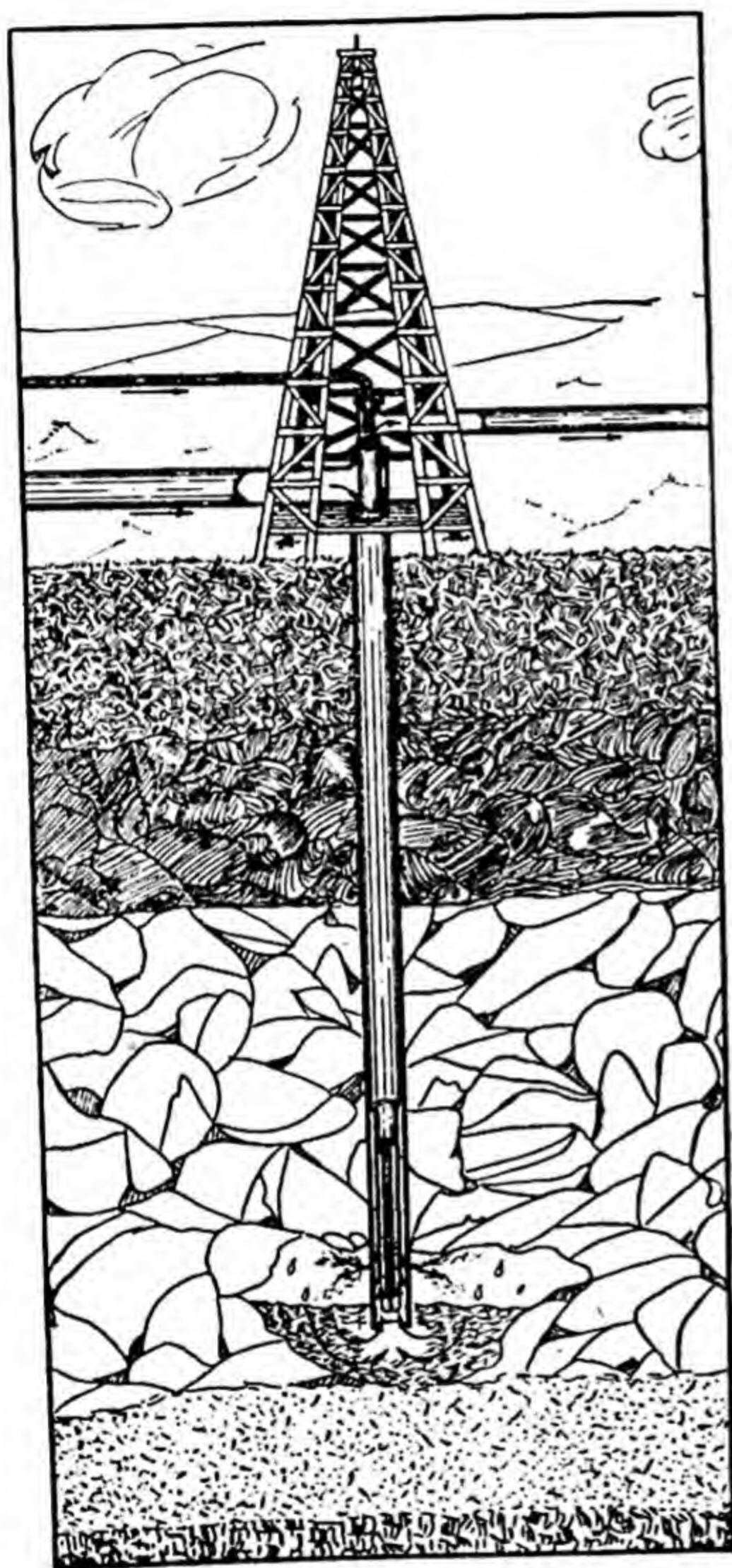


Fig. 148. The Frasch process for obtaining sulfur from underground deposits.

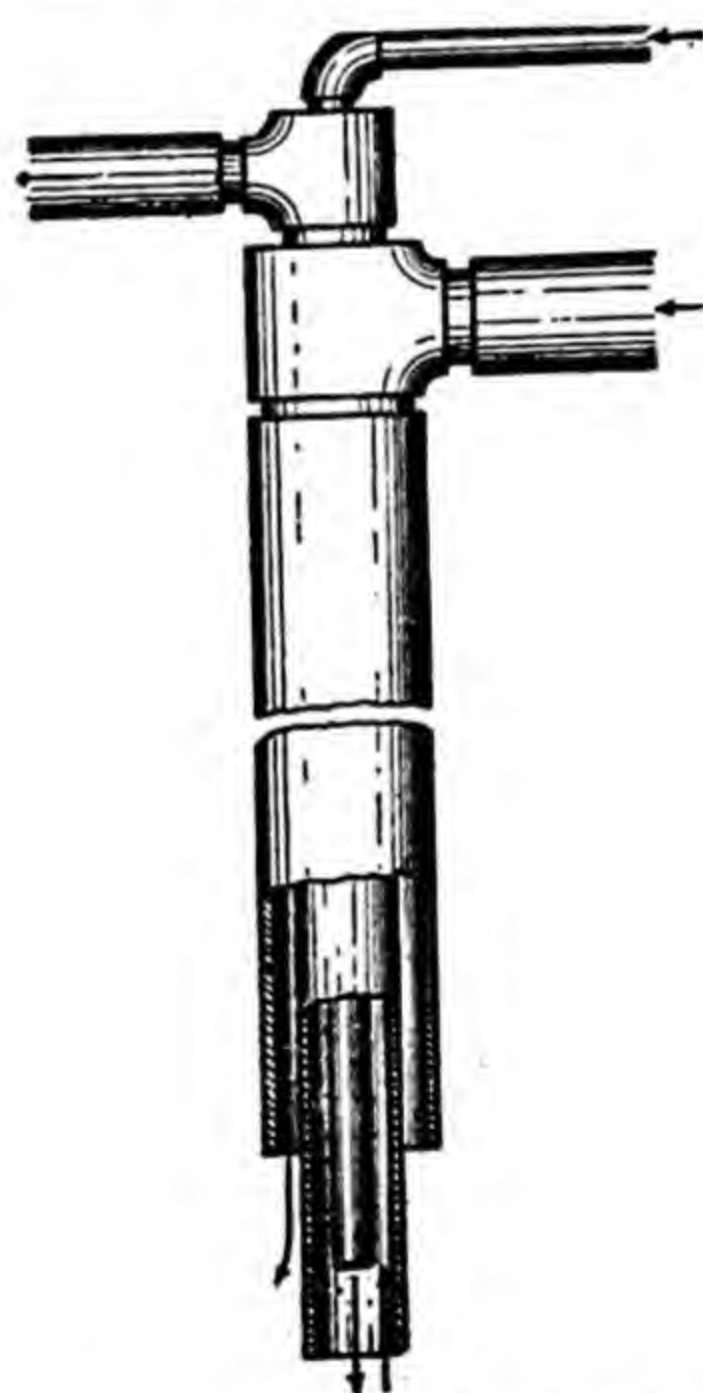


Fig. 149. A detail of the system of pipes used in the Frasch process.

matrix. The rock containing the sulfur is placed in large open-top kilns that have sloping floors. The heat produced by burning some of the sulfur melts the rest of it, and the molten sulfur is drawn from the bottom of the kiln and cast into molds. About one-third of the available sulfur is lost by this method of extraction.

In Louisiana and Texas many of the sulfur deposits lie several hundred feet below the surface of the ground. The mining

of these deposits was impossible until the ingenious method perfected by Frasch, an American chemical engineer, was adopted. This method consists of melting the sulfur in the deposit by means of water heated under pressure to 165°C . The frothy mixture of molten sulfur and water is forced to the surface by means of compressed air. From the diagram in Fig. 149 the details of the process may be followed. Hot water is forced down the outer pipe, and air is pumped down through the innermost pipe. The molten sulfur, mixed with hot water, is forced up through the space between the water pipe and the air pipe. At the surface the sulfur is pumped into huge bins, where it forms enormous, solid blocks. The sulfur thus obtained is nearly pure, and no further treatment is necessary.

Allotropic forms. Solid sulfur exists in several forms that differ from each other in physical properties. The allotropic forms which are capable of existing at room temperature are (1) rhombic or ordinary sulfur, (2) monoclinic sulfur, and (3) plastic sulfur. The atoms are all alike in all forms of sulfur, but in these three solid varieties of the element the atoms are arranged differently, giving rise to three kinds of sulfur molecules. Two of these are crystalline varieties.

Rhombic sulfur. Ordinary roll sulfur, when powdered, is readily soluble in carbon disulfide. When the carbon disulfide is allowed to evaporate from the solution at room temperature, the sulfur crystallizes in the form of regular octahedra (eight-sided crystals) having a melting point of 112.8°C . This is the rhombic form of the element. Ordinary solid or roll sulfur is composed of small crystals of the rhombic type.

Monoclinic or prismatic sulfur. When sulfur is melted at as low a temperature as possible (about 95°C .) and allowed to cool, it crystallizes in the form of long needles of a type called monoclinic crystals. In this form the sulfur atoms are grouped in a different way from that in the rhombic form. The melting point of monoclinic sulfur is 119.25°C . It is somewhat lighter (less dense) than the rhombic variety. At room temperature it slowly changes to the rhombic form.

Liquid and plastic sulfur. When ordinary crystalline sulfur is heated gently, it changes to a thin yellow liquid. If the heating is continued, the liquid becomes dark in color and viscous. These are two forms of liquid sulfur. The yellow variety is called S_{λ} , and the viscous liquid is called S_{μ} . Both forms are present in all liquid sulfur, but the amount of S_{μ} gradually increases with rising temperature. At 444.6°C ., the boiling point of sulfur, about 35 per cent of the liquid is in the form of S_{μ} . If this liquid is

cooled suddenly, by pouring it into a beaker of cold water, a rubber-like substance, called plastic sulfur, is obtained. It is a non-crystalline or amorphous form of sulfur. Unlike rhombic sulfur, it is not soluble in carbon disulfide. When amorphous sulfur is allowed to stand, it slowly hardens and changes to the stable rhombic form. Rhombic sulfur is composed of molecules having the formula S_8 , while S_μ consists of molecules containing six atoms, S_6 .

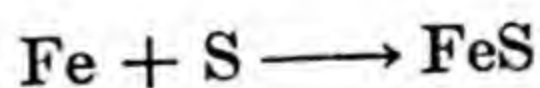
Sulfur vapor at the boiling point is composed largely of molecules having a formula of S_8 , but these are mixed with molecules of S_6 and S_2 .

Colloidal sulfur. Sulfur is soluble in an aqueous solution of sodium hydroxide or in an aqueous solution of sodium sulfide. When either of these solutions of sulfur is acidified, the sulfur precipitates in a very finely divided state. The particles are extremely small, and the sulfur in this form is known as *colloidal sulfur*. *Milk of sulfur* is made by shaking this precipitate with water.

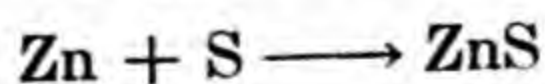
Flowers of sulfur. When sulfur is boiled, it changes to a yellow vapor, and if the vapor is suddenly cooled, it solidifies as a fine powder. In this treatment the sulfur crystallizes or becomes solid without going through the liquid state. The powdery mass formed in this way, called *flowers of sulfur*, consists of a mixture of the rhombic and amorphous forms.

Chemical properties of sulfur. Sulfur burns in the air, forming sulfur dioxide, SO_2 . It is a moderately active element, especially at high temperatures.

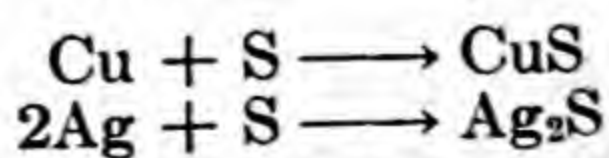
When a mixture of powdered iron and powdered sulfur is heated, the mass soon begins to glow, and it continues to do so after the burner is removed. The product formed is iron sulfide, FeS :



Powdered zinc combines with sulfur with almost explosive violence when the mixture is heated:



If a strip of copper or silver is placed in the vapor above the liquid in a tube of boiling sulfur, the metal becomes coated with a dark layer of the sulfide:



The tarnish which forms so easily on our silverware is silver sulfide. When a spoon is allowed to remain covered with the

yolk of an egg, it becomes black. The sulfur in the egg combines with the silver, forming a solid coating of silver sulfide. When we remove the tarnish from our silverware by polishing, we are actually scouring away part of the silver; that is, we remove the thin layer of silver sulfide.

There is a chemical process for cleaning tarnished silverware which is quicker than the use of silver polish and which removes no silver. Place the tarnished knives, forks, and spoons in an aluminum pan, allowing each piece of silver to be in direct contact with the aluminum. Cover the silverware with water and add to the water one teaspoonful of baking soda and one teaspoonful of common salt for each quart of water used. Place the pan on the kitchen stove or over a gas burner and heat it. Let the soda solution boil about one minute; then remove and dry the silver. Try it. A small amount of aluminum goes into solution as aluminum ions, Al^{+++} . This action leaves the pan negatively charged. The excess electrons flow from the pan to the silver and to the thin, dark-colored, silver sulfide film. The sulfur goes into solution as sulfide ions, S^{--} , leaving the silver bright and clean.

Uses of sulfur. Vast quantities of sulfur are used in the manufacture of sulfuric acid, in the making of matches, explosives, and fireworks, in the paper industry, and in vulcanizing rubber. It is used also as a component of some sprays for destroying fungi. Sulfur is one of the elements essential for plant growth.

Compounds of sulfur and oxygen. Since sulfur and oxygen are members of the same group in the Periodic Table, we should expect them to form similar compounds with other elements. (Both sulfur and oxygen require two electrons to complete the outer shell of eight.) A comparison of some of these compounds shows that the two elements are similar in properties.

FORMULAS OF SOME COMMON COMPOUNDS OF OXYGEN AND OF SULFUR

H_2O	H_2S	Ag_2O	Ag_2S
PbO	PbS	HgO	HgS
FeO	FeS	Na_2O	Na_2S
CuO	CuS		

Questions and Exercises

1. Explain the Frasch process for obtaining sulfur.
2. Would you expect silverware to tarnish more rapidly near an active volcano or in a region far from one?
3. How many grams of iron will be required to react with 128 g. of sulfur? How many grams of iron sulfide will be formed at the same time?
4. What is the use of the compressed air in the Frasch process?

5. How could you change rhombic sulfur into (a) amorphous sulfur; (b) flowers of sulfur; (c) monoclinic sulfur?
6. How could you convert amorphous sulfur into (a) rhombic sulfur; (b) monoclinic sulfur?
7. How is colloidal sulfur made?
8. How could you prove that the different allotropic forms of sulfur are actually composed of the same element?
9. Write eight equations to show similarity in chemical behavior between oxygen and sulfur.
10. Why does silverware tarnish so readily when left in a kitchen?

PART 2

The Sulfides

Hydrogen Sulfide

Occurrence. Hydrogen sulfide, a gas having the formula H_2S , is one of the products formed when an egg decays. It has the offensive odor of a bad egg. This gas is always one of the products formed when any organic matter containing sulfur decomposes. Hydrogen sulfide is present in the gases expelled by volcanoes during eruption, and it occurs in many mineral waters (sulfur springs) in regions of recent volcanic activity.

Preparation. Hydrogen sulfide may be prepared in small quantities by passing hydrogen and sulfur vapor

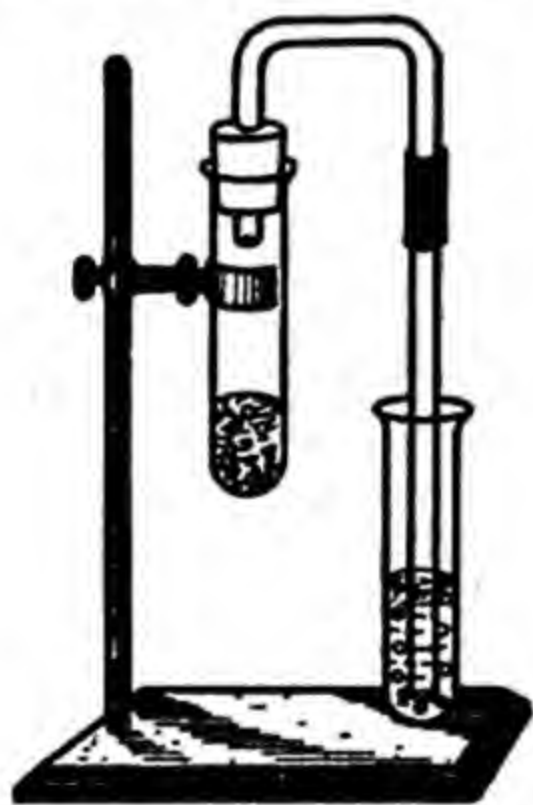


Fig. 150. A simple hydrogen sulfide generator.

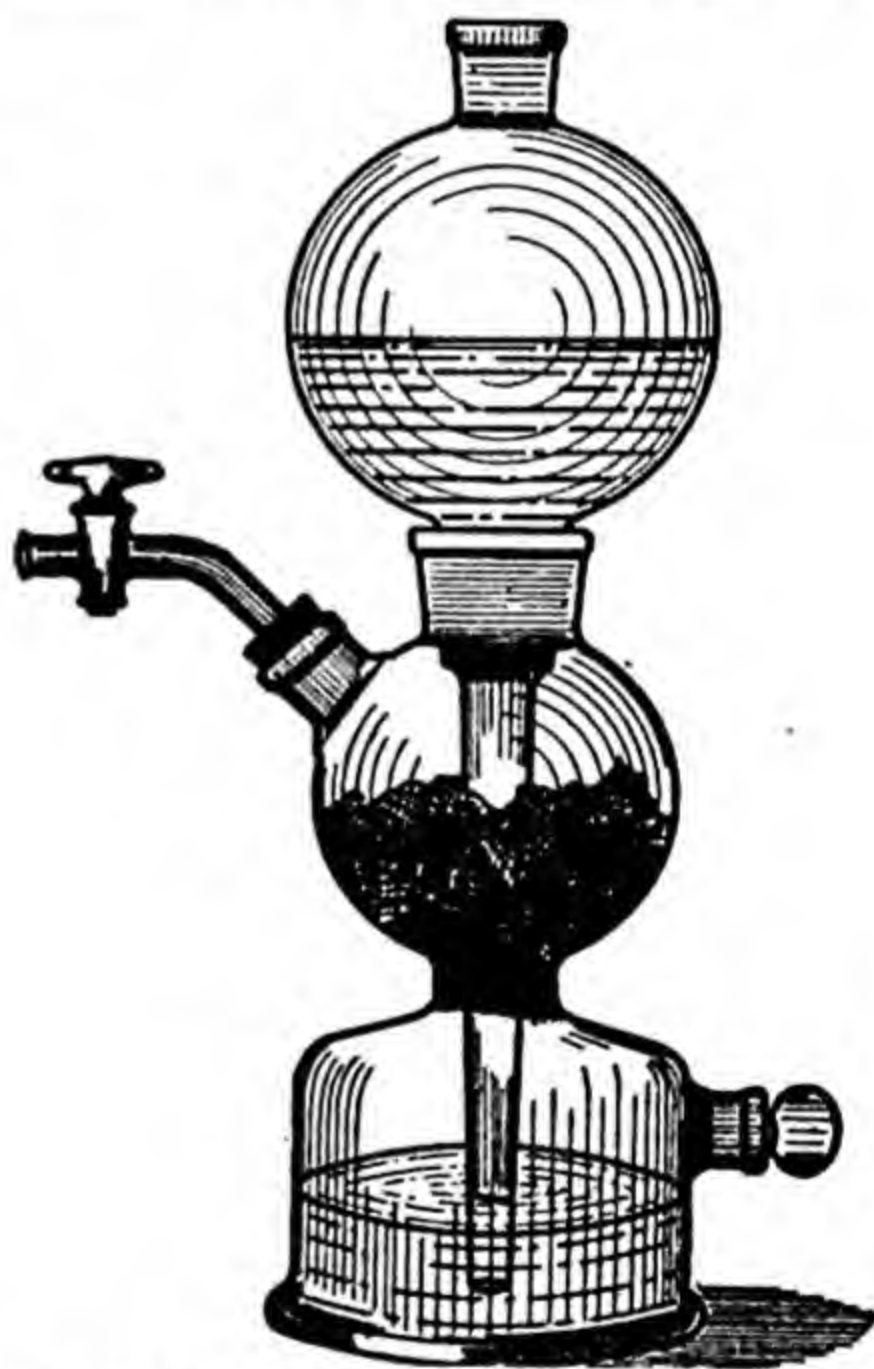
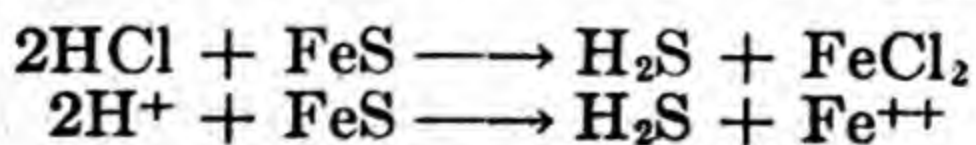


Fig. 151. Kipp's generator for the preparation of hydrogen sulfide.

through a red-hot tube, but the gas is more easily made by the action of dilute hydrochloric acid on ferrous sulfide:



(Ionic)

There are other sulfides which would do as well, but ferrous sulfide is generally used because it is inexpensive. When desired

in small quantities, hydrogen sulfide may be prepared by mixing ferrous sulfide and hydrochloric acid in a test tube as shown in Fig. 150.

Physical properties of hydrogen sulfide. Hydrogen sulfide is a colorless gas, somewhat heavier than air. It is slightly soluble in water. The aqueous solution is a weak acid, often called *hydrosulfuric acid*. Hydrogen sulfide is poisonous and, when breathed even in small quantities, produces headache; prolonged breathing of the gas may cause death. It is easily liquefied at room temperature by a pressure of 265 lb. per square inch. Liquid hydrogen sulfide in steel tanks or cylinders is available in many chemical laboratories.

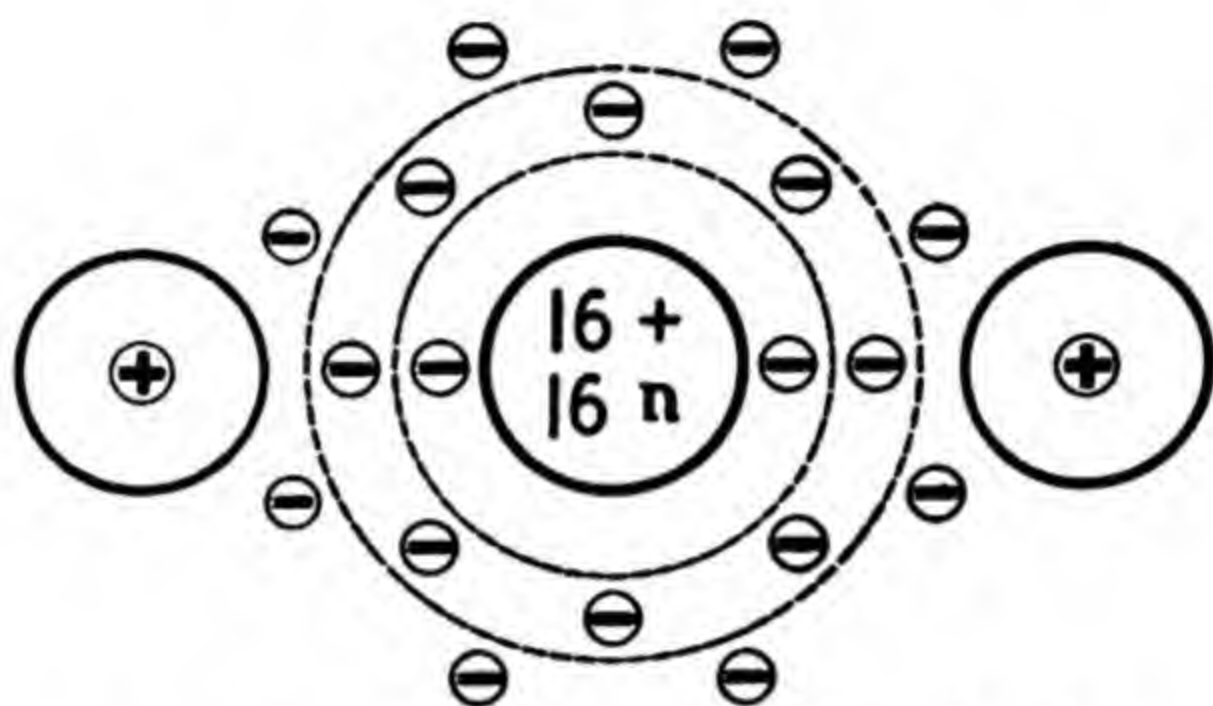
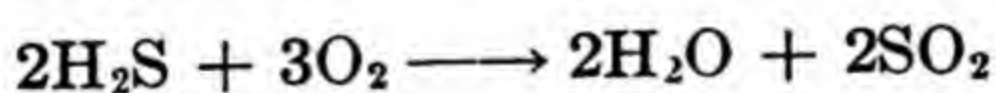


Fig. 152. A hydrogen sulfide molecule.

Chemical properties. Hydrogen sulfide is inflammable in air. When mixed with air in proper proportions and ignited, the mixture explodes, forming sulfur dioxide and water:



Hydrogen sulfide reacts with sulfur dioxide, forming water and free sulfur:



Since both hydrogen sulfide and sulfur dioxide pass into the atmosphere during volcanic eruptions, the deposits of sulfur found in regions of volcanic activity were probably formed in reactions between these gases, as indicated in the last equation.

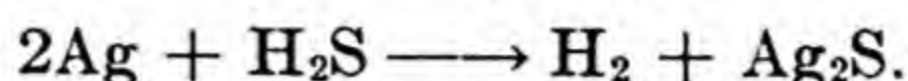
If in the burning of hydrogen sulfide an insufficient amount of oxygen is used, free sulfur is formed:



Other sulfides. All salts of hydrogen sulfide (or of hydrosulfuric acid) are called sulfides. We have learned that sulfides may be prepared by the direct combination of a metal with sulfur.

They may be prepared also from hydrogen sulfide in the following ways:

1. *By the action of hydrogen sulfide gas on metals:*

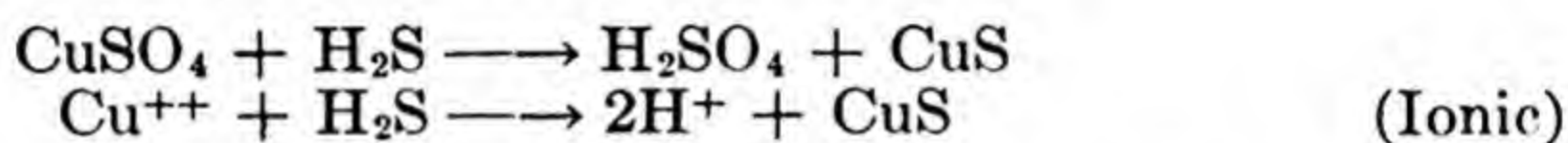


2. *By neutralizing aqueous solutions of the gas with hydroxides of the metals:*



The salt, in this case sodium sulfide, is obtained upon evaporation of the water from the solution.

3. *By passing hydrogen sulfide gas into salt solutions.* Most sulfides are insoluble, and because of this property they can be prepared from other salts by treatment with hydrogen sulfide. Thus, if hydrogen sulfide gas is passed into a solution of copper sulfate, the insoluble cupric sulfide precipitates:



Many of the sulfides have beautiful colors and are used as pigments. Cadmium sulfide, CdS , is the cadmium yellow which is used extensively by artists. Arsenic sulfide, As_2S_3 , also has a brilliant yellow color. Antimony sulfide, Sb_2S_3 , is used as an orange pigment. Tin sulfide, SnS_2 , is used in gilt paint. Lead sulfide is black. Zinc sulfide, which is white, is used for painting buildings and laboratories where hydrogen sulfide fumes may come in contact with the paint. Ordinary white paint, which is composed largely of compounds of lead, rapidly darkens under these conditions.

Uses of sulfides. Hydrogen sulfide is one of the reagents used by the chemist in analyzing unknown substances containing metals. In many cases identification can be made by observing the color of the sulfide formed when hydrogen sulfide is passed into a solution, and by the solubility of the precipitated sulfide in various reagents. Some sulfides are soluble in water. Others are insoluble in water but soluble in hydrochloric acid. Some are insoluble in hydrochloric acid but soluble in nitric acid, and others are soluble only in aqua regia. Aqua regia ("royal water") is a mixture of concentrated nitric acid and concentrated hydrochloric acid. On account of these differences in solubilities, many sulfides are easily identified.

Questions and Exercises

1. What is formed when (a) sulfur burns in air, (b) sulfur and zinc are heated together, (c) sulfur and copper are heated together, (d) sulfur dioxide and hydro-

gen sulfide react, (e) hydrogen sulfide is passed into a copper sulfate solution, (f) hydrogen sulfide reacts with oxygen?

2. Beginning with hydrochloric acid, iron, and sulfur, explain how you could prepare hydrogen sulfide.

3. In collecting H_2S by the displacement of air, would you hold the container right side up, or would you invert it?

4. Give two methods of making silver sulfide, Ag_2S .

5. Zinc sulfide, ZnS , is soluble, and copper sulfide, CuS , is insoluble, in hydrochloric acid. How would you remove the copper from a solution containing zinc sulfate, ZnSO_4 , and copper sulfate, CuSO_4 ?

6. What are the properties of hydrogen sulfide?

7. What is the weight of 22.4 liters of H_2S gas at 0°C . and 1 atmosphere pressure? What is the weight of the same volume of air under the same conditions?

8. The formula for hydrated copper sulfate is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. If 12 g. of a crude sample containing this salt gave 3.84 g. of CuS upon precipitation with H_2S , what percentage of the sample was $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$? (Ans. 80 per cent.)

9. Beginning with free sulfur and any necessary reagents, outline methods for making the following compounds:

- | | | |
|--------------------------|---------------------------|---------------------------|
| (a) H_2S | (c) Cu_2S | (e) ZnS |
| (b) FeS | (d) CuS | (f) Na_2S |

10. How could you distinguish between zinc sulfide and ferrous sulfide? (See table, Properties of Sulfides, page 515.)

11. Draw an electronic picture of a molecule of sodium sulfide. Include only the valence electrons in the picture. Sodium has one electron in the valence shell and sulfur has six valence electrons. Sulfur has a greater tendency to acquire and hold electrons than has sodium.

12. Ferrous sulfide, FeS , and copper sulfide, CuS , are both black powders. Devise a means of distinguishing them. (Consult table, Properties of Sulfides, page 515.)

13. Calculate the weight of 1 liter of hydrogen sulfide under standard conditions.

14. How many liters of oxygen will be required to burn completely 10 liters of hydrogen sulfide?

15. Calculate the percentage composition of hydrogen sulfide.

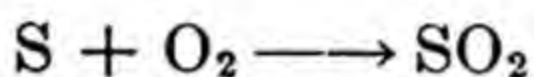
16. The water of a sulfur spring does not have a sour taste. Would you conclude that hydrosulfuric acid is a strong or a weak acid?

PART 3

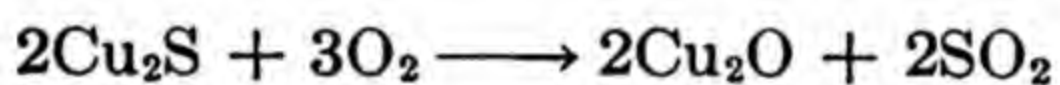
Oxides and Acids of Sulfur

Sulfur forms two important oxides, sulfur dioxide and sulfur trioxide. These oxides are the anhydrides of sulfurous acid and sulfuric acid, respectively.

Sulfur dioxide is formed when sulfur burns in the air or in oxygen:



It is produced also during the smelting of sulfide ores. Many of the common metals occur in nature as sulfides. The first step in producing the free metal consists in roasting the ore in air. The sulfur burns to sulfur dioxide, changing the ore to the oxide, which can then be reduced:



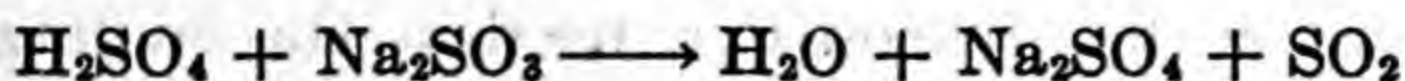
When the fumes from the smelter are allowed to escape into the air, crops in the vicinity may be destroyed, for sulfur dioxide has a destructive effect on all vegetation.

Sulfur dioxide, like hydrogen sulfide, is found also in regions of general volcanic activity. The air of cities contains some sulfur dioxide, which is produced by the burning of sulfur compounds present in coal, crude oil, and gas. The chimneys of large cities like New York and Chicago emit hundreds of tons of sulfur dioxide daily.

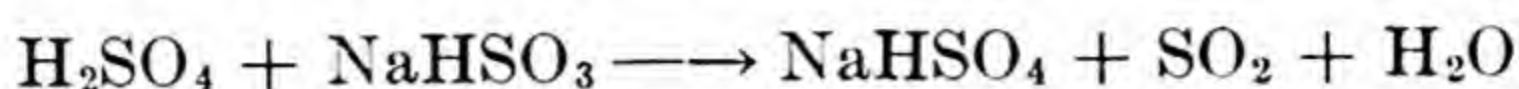
Preparation of sulfur dioxide. Sulfur dioxide is prepared on a large scale by burning sulfur in air:



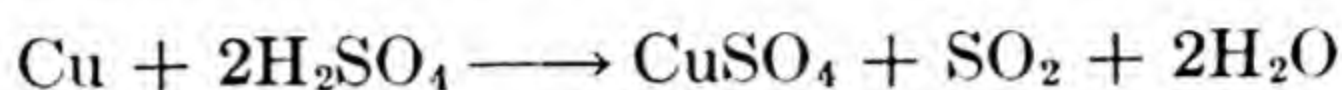
In the laboratory where convenience rather than economy is the chief consideration, sulfur dioxide is prepared by dropping dilute sulfuric acid on solid sodium sulfite or into a solution of sodium sulfite:



The reaction may be carried out also by using sodium hydrogen sulfite instead of the normal salt:



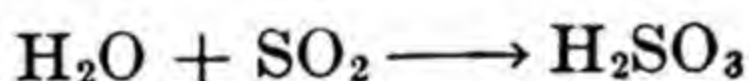
Sulfur dioxide may also be prepared in the laboratory by the action of concentrated sulfuric acid on copper:



Physical properties of sulfur dioxide. Sulfur dioxide is a colorless gas with the very pungent odor which is characteristic of burning sulfur. It is 2.2 times as heavy as air. It is very soluble in water, one volume of water dissolving about 80 volumes of the gas at the ordinary temperature of the laboratory.

Sulfur dioxide is rather easily liquefied. The liquid boils at -10°C ., so if the gas is cooled to this temperature or lower, it liquefies under atmospheric pressure. At 20°C . the gas liquefies under 3 atmospheres of pressure. One atmosphere of pressure is equal to 15 lb. per square inch.

Chemical properties of sulfur dioxide. Sulfur dioxide combines with oxygen (but not readily under ordinary conditions) to form sulfur trioxide, SO_3 . The water solution of sulfur dioxide turns blue litmus red, indicating that the solution is acidic. The weak sulfurous acid, H_2SO_3 , is formed in a reaction between sulfur dioxide and water:



Sulfurous acid exists only in solution. When the solvent is evaporated, the acid decomposes, yielding water and sulfur dioxide. Salts of this acid are called *sulfites*. These salts are stable, and they are available in the laboratory in crystalline form. Sodium sulfite is made by neutralizing sulfurous acid with sodium hydroxide:



Sulfur dioxide, under certain conditions, removes oxygen from other substances. It is therefore a reducing agent. Under other conditions it may act as an oxidizing agent.

Uses of sulfur dioxide. Sulfur dioxide is employed in the bleaching of silk, wool, straw, paper, vegetables, fruits, and nuts. Its bleaching action is less injurious but also less permanent than the bleaching accomplished by the use of chlorine. It is a fungicide and an insecticide, and therefore its use in treating fruits and nuts serves more than one purpose. Sulfur dioxide is easily liquefied, and for that reason it is used as the cooling medium in

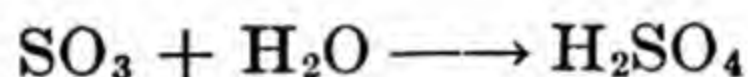
many electrical household refrigerators. When liquid sulfur dioxide is allowed to vaporize in the refrigerating unit, it absorbs heat from the surroundings, producing a cooling effect. The gas must then be compressed and liquefied again. Compression causes it to get warm, but this part of the cycle takes place in the coils outside the cabinet, and the heat produced is conveyed away by the air surrounding the coils.

The most important use of sulfur dioxide is in the manufacture of sulfuric acid.

Sulfur Trioxide

Preparation. Only a trace of sulfur trioxide, SO_3 , is formed when sulfur burns in air. The product formed is the dioxide. When pure sulfur dioxide and oxygen are heated together for several hours, they combine so slowly that only a small amount of the trioxide is formed. If, however, a suitable catalyst is present, such as finely divided platinum, the reaction is rapid.

Properties. Sulfur trioxide is a gas at the temperature used in making it, but it can be condensed to a liquid, boiling at 46°C ., or by further cooling it can be converted into a white crystalline solid. It dissolves in water with the liberation of a great amount of heat, forming sulfuric acid:



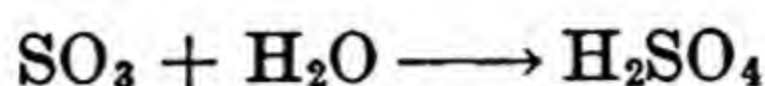
Sulfur trioxide is the anhydride of sulfuric acid. Thousands of tons of the oxide are manufactured each year to be used in making sulfuric acid.

The Manufacture of Sulfuric Acid

The oxidation of sulfur dioxide to sulfur trioxide is accomplished on a commercial scale by the *contact process* or by the *chamber process*.

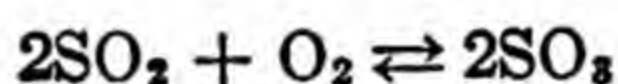
The contact process. Either platinum or a mixture composed of vanadium compounds is used as a catalyst in the contact process of making sulfuric acid. Sulfur dioxide is made by burning sulfur. Then the sulfur dioxide and oxygen are brought in contact with each other on the surface of the catalyst. These gases are rendered more active when adsorbed on the surface of the catalyst, and they combine rapidly at a temperature as low as 400°C . Since platinum is very expensive, it is used in a finely divided state, so that a small weight of the metal covers a large surface. Asbestos is soaked in a solution containing a platinum salt, then heated to decompose the salt. Fine particles of pure platinum then cover the surface of the asbestos. The sulfur trioxide formed by the

union of the sulfur dioxide and oxygen is a vapor at the temperature used. The vapor is conducted into water, forming sulfuric acid of any desired strength:



This process has the advantage of requiring relatively little space, and it can be used to produce concentrated acid. It has the disadvantage of requiring very pure sulfur dioxide. Small amounts of impurities, particularly arsenic, render the platinum catalyst inactive. Vanadium is cheaper than platinum, and the vanadium compounds used in sulfuric acid plants are not so sensitive to the presence of arsenic. This new contact agent has been substituted for platinum in several plants.

Why is a catalyst necessary? The reaction between sulfur dioxide and oxygen is a reversible process:



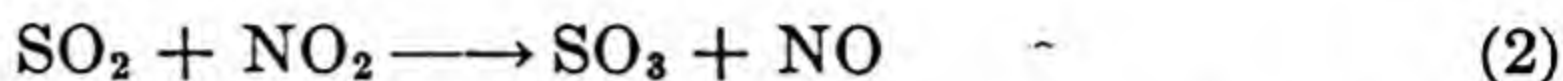
At low temperatures the reaction goes almost exclusively from left to right, forming SO_3 , but the reaction is extremely slow. At very high temperatures the reaction is rapid, but the SO_3 decomposes almost as fast as it is formed. If sulfur dioxide and oxygen at 20°C . were mixed in proper proportions in a closed vessel, they would, in time, be converted almost completely into sulfur trioxide, but the reaction is so slow that it would require several years to complete it. When the temperature is raised to 800°C ., the reaction becomes rapid, but at 800°C . the SO_3 is decomposed so rapidly that only 30 per cent of the sulfur dioxide is converted into the trioxide. It is desirable, therefore, to find some means of increasing the rate of the reaction at moderately low temperatures. This acceleration is accomplished by bringing the sulfur dioxide and oxygen in contact with a catalyst which increases the speed of the reaction between the two gases and which is itself not destroyed in the process. At 400°C . the gases combine rapidly when in contact with platinum, and at this temperature there is very little decomposition of the sulfur trioxide.

The chamber process. In the chamber process for making sulfuric acid the catalyst used is nitric oxide, a colorless gas made from nitric acid. The reaction takes place in huge chambers which contain the reacting gases, SO_2 , O_2 , NO , and water vapor. The chambers are lined with lead, which withstands the corrosive action of these gases.

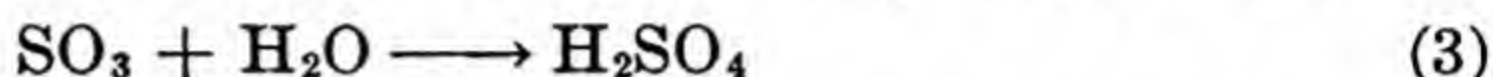
Nitric oxide, NO, reacts with oxygen to form nitrogen dioxide, NO₂, which is a brown gas:



The nitrogen dioxide then reacts with sulfur dioxide to produce sulfur trioxide and nitric oxide:



Sulfur trioxide combines with steam, forming sulfuric acid:

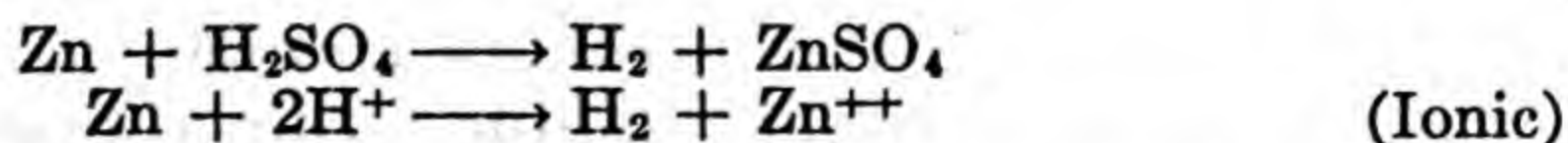


The NO formed in the second stage of the process unites with oxygen and is returned to the chamber as NO₂ to be used again. Some more complicated reactions occur, but those given above show the principal features of the chamber process.

Physical and chemical properties of sulfuric acid. Sulfuric acid is a heavy, oily liquid. It is often called *oil of vitriol*. The pure acid is about twice as heavy as water. Its boiling point is high (98 per cent acid boils at 338°C.) and, therefore, it can be used in the manufacture of lower-boiling-point acids from salts of these acids. It is used in large quantities in the manufacture of hydrochloric acid and nitric acid.

Sulfuric acid dissolves in water with an evolution of heat. It is always advisable to stir the water vigorously while adding sulfuric acid to it, and *the acid should always be added to the water and not the water to the acid*. When water is added to concentrated sulfuric acid, mixing does not occur rapidly and, through local heating, steam is formed. A puff or explosion produced by escaping steam spatters acid in all directions. Sulfuric acid combines with water so readily that it actually takes water away from other substances. Sugar contains carbon, hydrogen, and oxygen, the hydrogen and oxygen atoms existing in the ratio of 2 to 1, as in water. Concentrated sulfuric acid removes hydrogen and oxygen from sugar, and free carbon is formed. In the same way concentrated sulfuric acid causes wood to char. When the acid is spilled on the flesh, it causes a serious burn because of this dehydrating action.

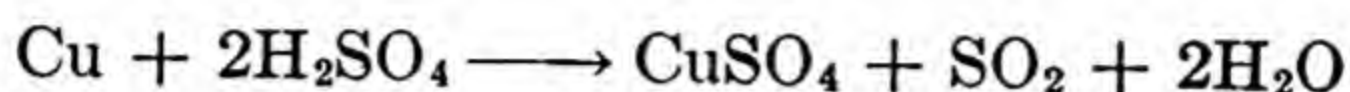
Action of sulfuric acid on metals. Dilute sulfuric acid reacts with aluminum, zinc, iron, or tin to yield hydrogen and a sulfate of the metal:



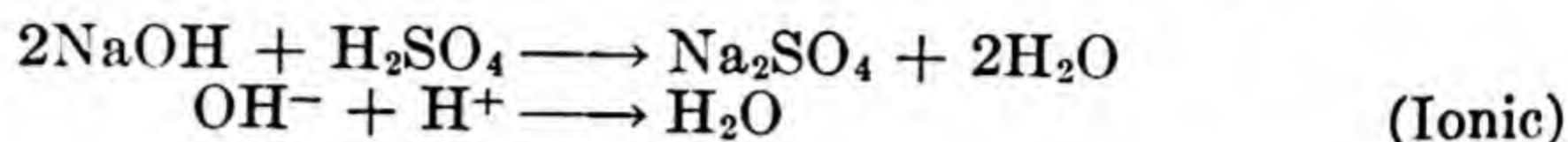
The dilute acid does not react with copper, mercury, or silver. Hot concentrated sulfuric acid dissolves these metals, but hydrogen

is not evolved. Sulfuric acid oxidizes these metals. Sulfur dioxide is liberated through reduction of part of the acid.

The reaction may be represented by the equation:



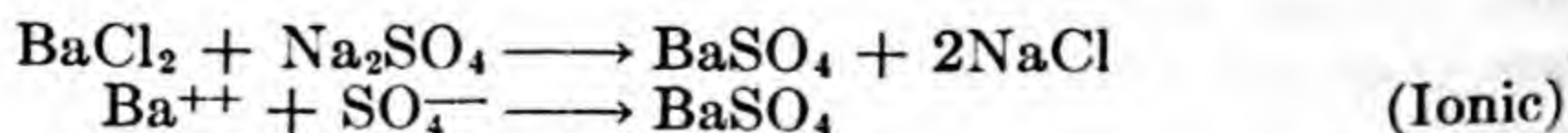
Sulfuric acid, like other acids, can be neutralized by bases:



The uses of sulfuric acid. Sulfuric acid is more extensively employed in industrial processes than any other chemical. It has often been said that the degree of industrial development of any country may be judged by the amount of sulfuric acid it consumes.

It was mentioned above that sulfuric acid is used in the manufacture of nitric acid, hydrochloric acid, and hydrogen peroxide. It is used also in the manufacture of phosphate fertilizer. More than 2,500,000 tons of the acid are used annually for this purpose alone in the United States. Almost the same amount is used in the refining of gasoline and other petroleum products. Sulphuric acid removes water and some other undesirable substances from petroleum. The steel industry uses sulfuric acid to a large extent. Iron and steel are cleaned, or pickled, by treatment with this acid. The acid is employed extensively in the manufacture of ammonium sulfate, explosives, and rayon. Lead storage batteries account for the use of many thousands of tons of sulfuric acid annually.

Test for the sulfate ion. The sulfate ion SO_4^{--} , reacts with the barium ion, Ba^{++} , to produce an insoluble compound, barium sulfate, BaSO_4 . A test for a *soluble sulfate* is made by adding a solution containing Ba^{++} ions to a solution of the substance to be tested. Barium chloride is the reagent generally used to test for a sulfate:



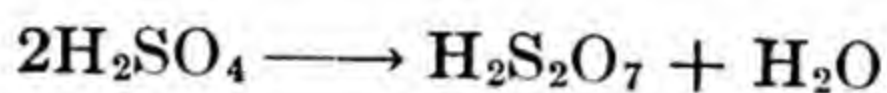
The barium sulfate formed in the reaction appears as a white precipitate which is insoluble in water and also insoluble in acids. Barium carbonate, the white precipitate formed when barium chloride is added to a solution containing carbonate ions, also is insoluble in water, but it is soluble in acids.

Other acids of sulfur. Sulfur forms a large number of acids in addition to sulfurous and sulfuric acids. The formulas and names of a few of these acids are given in the following table:

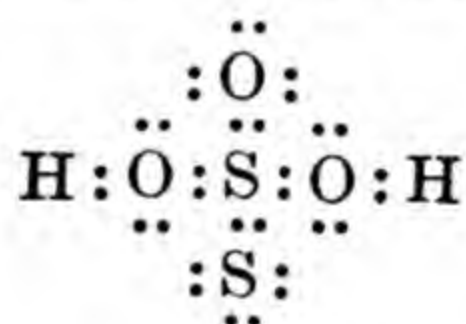
Name of acid	Formula	Name of acid	Formula
Hyposulfurous acid.....	$\text{H}_2\text{S}_2\text{O}_4$	Trithionic acid.....	$\text{H}_2\text{S}_3\text{O}_6$
Thiosulfuric acid.....	$\text{H}_2\text{S}_2\text{O}_3$	Tetrathionic acid.....	$\text{H}_2\text{S}_4\text{O}_6$
Hydrogen polysulfide.....	H_2S_4	Pyrosulfuric acid.....	$\text{H}_2\text{S}_2\text{O}_7$
Dithionic acid.....	$\text{H}_2\text{S}_2\text{O}_6$	Persulfuric acid.....	$\text{H}_2\text{S}_2\text{O}_8$

Pyrosulfuric acid is formed when sulfur trioxide is dissolved in concentrated sulfuric acid. If allowed to stand in an open container it decomposes, giving off dense fumes of sulfur trioxide. It is often called fuming sulfuric acid, or oleum.

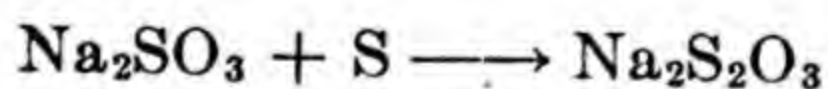
Pyrosulfuric acid may be considered as a compound, derived from two molecules of sulfuric acid through the loss of one molecule of water.



Thiosulfuric acid is similar in structure to sulfuric acid, but has an atom of sulfur in place of one of the oxygen atoms. Its electronic formula is written as follows:



Thiosulfuric acid has not been obtained in the pure condition, but its salts are stable and well-known. The "hypo" used by photographers is sodium thiosulfate. It is made by boiling sulfur with an alkaline solution of sodium sulfite, then evaporating the water from the solution:

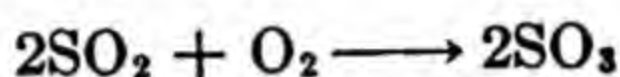


In addition to its use in photography, sodium thiosulfate is used in the textile and paper industries to remove the excess of chlorine used in bleaching. It is employed also in some metallurgical processes.

Questions and Exercises

1. Describe sulfur dioxide.
2. What is sulfurous acid?
3. Is sulfurous acid a strong or a weak acid?
4. What is meant by the terms *strong* and *weak* as applied to acids?
5. (a) Why is sulfuric acid used to release sulfur dioxide from a sulfite?
(b) Could hydrochloric acid be used in its place? (c) Nitric acid?

6. Write equations representing two methods for making sulfur dioxide.
7. What is the anhydride of sulfurous acid?
8. What weight of sodium sulfite must be dissolved in sulfuric acid to liberate 10 liters of sulfur dioxide, the gas to be measured at 0°C. and 1 atmosphere pressure?
9. What weight of sodium hydrogen sulfite (sodium bisulfite) must be dissolved in sulfuric acid to liberate 100 g. of sulfur dioxide?
10. What is the weight of 1 liter of sulfur dioxide under standard conditions?
11. What is the weight of 22.4 liters of sulfur dioxide under standard conditions. Is it lighter or heavier than air?
12. How many liters of oxygen will combine with 10 liters of SO_2 in the following reaction?



Assume that all the gases are measured under standard conditions.

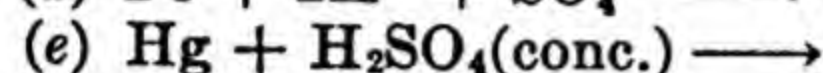
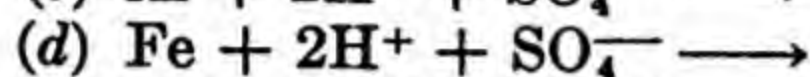
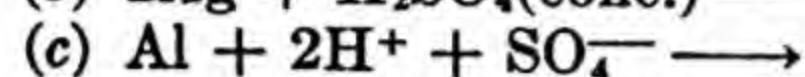
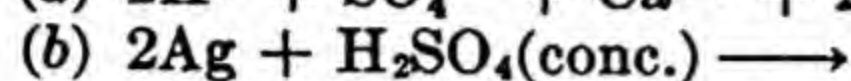
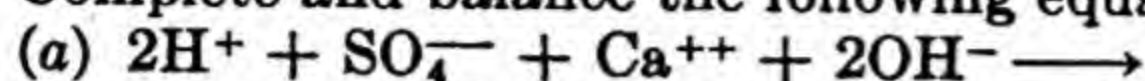
13. Mention five uses of sulfur dioxide.
14. Why is not sulfur dioxide collected over water in the same way that oxygen is collected?
15. How would you proceed to bleach a straw hat?
16. Describe sulfur trioxide.
17. Describe the two methods for converting sulfur dioxide into sulfur trioxide.
18. Write equations for the contact process for making sulfuric acid, beginning with sulfur.
19. What is a catalyst? Name five catalysts that have been referred to in this course.
20. Given two solutions, one of which contains sodium sulfate and the other sulfuric acid: what test would you use to distinguish between the two solutions?
21. Outline a method for the manufacture of sulfuric acid, using an ore containing zinc sulfide as the source of the sulfur.
22. What weight of sulfuric acid could be made from 1 ton of pure sulfur?
23. How much sulfuric acid must be used to neutralize 1 lb. of sodium hydroxide?
24. Calculate the weight of sulfuric acid necessary to produce 1 ton of copper sulfate or blue vitriol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, from pure copper.
25. A solution containing 5 g. of barium chloride was added to a solution containing 3 g. of potassium sulfate. Calculate the weight of the precipitate formed. Which of the two reagents (BaCl_2 and K_2SO_4) was present in excess?
26. What weight of barium sulfate would be precipitated if an excess of barium chloride were added to a solution containing 5 g. of ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$?
27. Given three separate solutions, one containing sodium carbonate, another containing sodium sulfate, and a third containing a mixture of sodium carbonate and sodium sulfate: how would you determine which solution contained the

sodium carbonate alone; which the sodium sulfate alone; and which the mixture of the two salts?

28. Calculate the percentage composition of sulfuric acid.

29. Give two examples of metals that react with dilute sulfuric acid, and two that do not.

30. Complete and balance the following equations:



31. Name three uses of sulfuric acid and the property of the acid that makes each use possible.

32. How many liters of air must be used to supply the oxygen required to convert 1000 liters of sulfur dioxide into sulfur trioxide? Consider all gases under standard conditions.

33. What is (a) muriatic acid; (b) aqua regia; (c) oil of vitriol?

PART 4

Selenium and Tellurium and Their Compounds

Selenium

Selenium closely resembles sulfur in many of its properties. The two elements form very similar compounds. Selenium was discovered in 1817 by Berzelius, who gave it the name it now bears, meaning "the moon."

Occurrence. The element is frequently found in small quantities in sulfur deposits. It is found also combined with many of the metals, especially copper, silver, and lead. When sulfur or metal sulfides containing selenium are used in the manufacture of sulfuric acid, some selenium is always found in the flue dust as well as in the residues which collect in the lead chambers.

Properties. Selenium occurs in three crystalline, allotropic forms. Two of these are red, monoclinic forms, while the third is gray in color. The latter is formed by rapidly cooling liquid selenium. The gray form has an interesting property of being a much better conductor of electricity in the light than it is in the dark. The element has been used in devices for measuring the intensity of the light of the stars, for automatically turning on lights at night and turning them off in the morning, and for the transmission of pictures by telegraph.

In some limited areas selenium compounds occur in the soil in considerable concentrations. These compounds are absorbed by plants in sufficient quantities to poison cattle that eat the plants.

Compounds of selenium. The compounds of selenium resemble those of sulfur in composition as well as in properties. Hydrogen selenide, H_2Se , is a gas with a very disagreeable odor, which dissolves in water to form an acid, slightly stronger than the corresponding acid of sulfur. Selenium dioxide, SeO_2 , is a white crystalline solid, formed when selenium burns in air. When dissolved in water, it forms the weak selenious acid, H_2SeO_3 . Selenic acid, H_2SeO_4 , resembles sulfuric acid in chemical properties. The salts formed from the three acids, namely, the selenides, selenites, and selenates, resemble the corresponding salts of the sulfur acids, the sulfides, sulfites and sulfates.

Uses. The element selenium is used in making red glass, such as that used for railroad signals. It is used also in the manufacture of colorless glass from sand containing ferrous silicate, which otherwise yields greenish glass. A little selenium neutralizes the green color which ferrous silicate alone produces. Selenium compounds have been used to some extent as insect sprays in fruit orchards.

Tellurium

Tellurium was discovered near the close of the eighteenth century. Its name is derived from the Greek word meaning "the earth." Tellurium does not show a marked similarity to sulfur but the two elements do form analogous compounds.

Occurrence and properties. Tellurium is rarely found free in nature. It occurs chiefly as the tellurides of copper, lead, silver, gold, iron, and bismuth. It is usually obtained from the residues in electrolytic copper refining.

Tellurium is somewhat metallic in appearance, resembling antimony. It occurs in two crystalline allotropic forms, one, a grey rhombohedral form, and another modification about which little is known. An amorphous form is precipitated in a manner similar to that used for making amorphous sulfur and selenium. The amorphous form changes back to the crystalline form very slowly at ordinary temperatures, but rapidly at temperatures near the melting point of the element. The metallic form is insoluble in carbon disulfide. Tellurium is the poorest conductor of electricity of all of the metals. Tellurium has often been called the useless metal. It is gradually developing into a useful component of the alloys of iron and lead.

Compounds of tellurium. Hydrogen telluride, H_2Te , is a gas with a very disagreeable odor, which resembles hydrogen sulfide. Its water solution is a weak acid. Tellurium dioxide, TeO_2 , is readily formed when tellurium burns in the air. Tellurium trioxide, TeO_3 , is an orange-colored solid formed by carefully heating the acid of which it is the anhydride, telluric acid, H_2TeO_4 . Salts derived from the various acids of tellurium are stable compounds. They resemble the corresponding salts of sulfur and of selenium.

UNIT XI

Group II of the Periodic Table: Beryllium, Magnesium, Calcium, Strontium, Barium, and Radium

PART 1

Beryllium and Magnesium

We shall now study the elements which make up the second main group of the Periodic System. These elements, known as the alkaline earth metals, are beryllium, magnesium, calcium, strontium, barium, and radium. Since each has two valence electrons, their chemical properties are similar. When they react with other elements, they give up their two valence electrons. Therefore the ion of each of these elements has two positive charges: Be^{++} , Mg^{++} , Ca^{++} , Sr^{++} , Ba^{++} , Ra^{++} .

Second
main
group

Be
Mg
Ca
Sr
Ba
Ra

Magnesium and calcium are the most important members of the group. Like the alkali metals, the elements of Group II are all too reactive to exist in nature in the free state.

Beryllium, because of the small size of its atom, does not give up electrons as readily as do the other members of this group. When the valence electrons of an atom are as close to the positively charged nucleus as they are in the beryllium atom, there is a tendency for the atom to share electrons rather than to yield them entirely to another atom.

The principal physical constants of the members of Group II are contained in the table on page 345.

Beryllium

Occurrence and properties. Beryllium does not exist in the free state in nature, but is found in small amounts in the form of its compounds in many minerals. The most important mineral is beryl, $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. When beryl contains enough chromium to color it a bright green it is known as emerald. Aquamarines have the same composition, but are colored a light greenish blue. Much beryl is found in New Hampshire; pieces weighing

as much as a ton have been found there. The element beryllium is metallic, and is silvery white in appearance. It is hard enough to scratch glass, and it is a good conductor of the electric current. The metal is usually prepared by the electrolysis of the melted halides, or by the reduction of beryllium chloride with sodium or potassium at a very high temperature.

	Be	Mg	Ca	Sr	Ba	Ra
Atomic number.....	4	12	20	38	56	88
Atomic weight.....	9.02	24.32	40.8	87.63	137.36	226.05
Electron structure:						
1st shell.....	2	2	2	2	2	2
2nd shell.....	2	8	8	8	8	8
3rd shell.....	—	2	8	18	18	18
4th shell.....	—	—	2	8	18	32
5th shell.....	—	—	—	2	8	18
6th shell.....	—	—	—	—	2	8
7th shell.....	—	—	—	—	—	2
Isotopes.....	9	{ 24, 25, 26	{ 40, 44, 42, 43, 46, 48	{ 88, 86, 84, 87, 90	{ 138, 136, 134, 137, 135, 132	226
Melting point, °C.....	1300	650	851	757	850	960
Boiling point, °C.....	1500	1107	1487	1384	1640	1140
Density, grams per cubic centimeter.....	1.73	1.75	1.55	2.6	3.75	6.0

Beryllium does not react readily with water, due to the formation of a protective film of beryllium oxide on the surface of the metal. It reacts with dilute acids, and with alkalies, liberating hydrogen.

Uses of beryllium. Beryllium metal alone has no important uses, but it is an important constituent of some alloys. It adds hardness and strength to other metals, especially to copper. The chief alloy of beryllium is one with copper, containing 2.25 per cent of beryllium. This alloy can be treated with heat so as to produce springs which have high resilience and resistance to fatigue, wear, and corrosion. An alloy of beryllium with nickel makes a smooth bearing metal with a high melting point which is especially adapted to use in airplane engines. A small amount of beryllium is used in making certain varieties of rustless steel.

Magnesium

Occurrence. Magnesium is never found free in nature. It occurs in many compounds, however, in the crust of the earth. Nearly all of the silicate rocks contain magnesium. The element

is found also as the carbonate. The mineral magnesite is impure magnesium carbonate, MgCO_3 ; and dolomite is a double carbonate of calcium and magnesium, $\text{MgCO}_3 \cdot \text{CaCO}_3$. Talc, or soapstone, and asbestos are complex silicates containing magnesium, having the formulas $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ and $\text{CaMg}_3(\text{SiO}_3)_4$ respectively. Car-

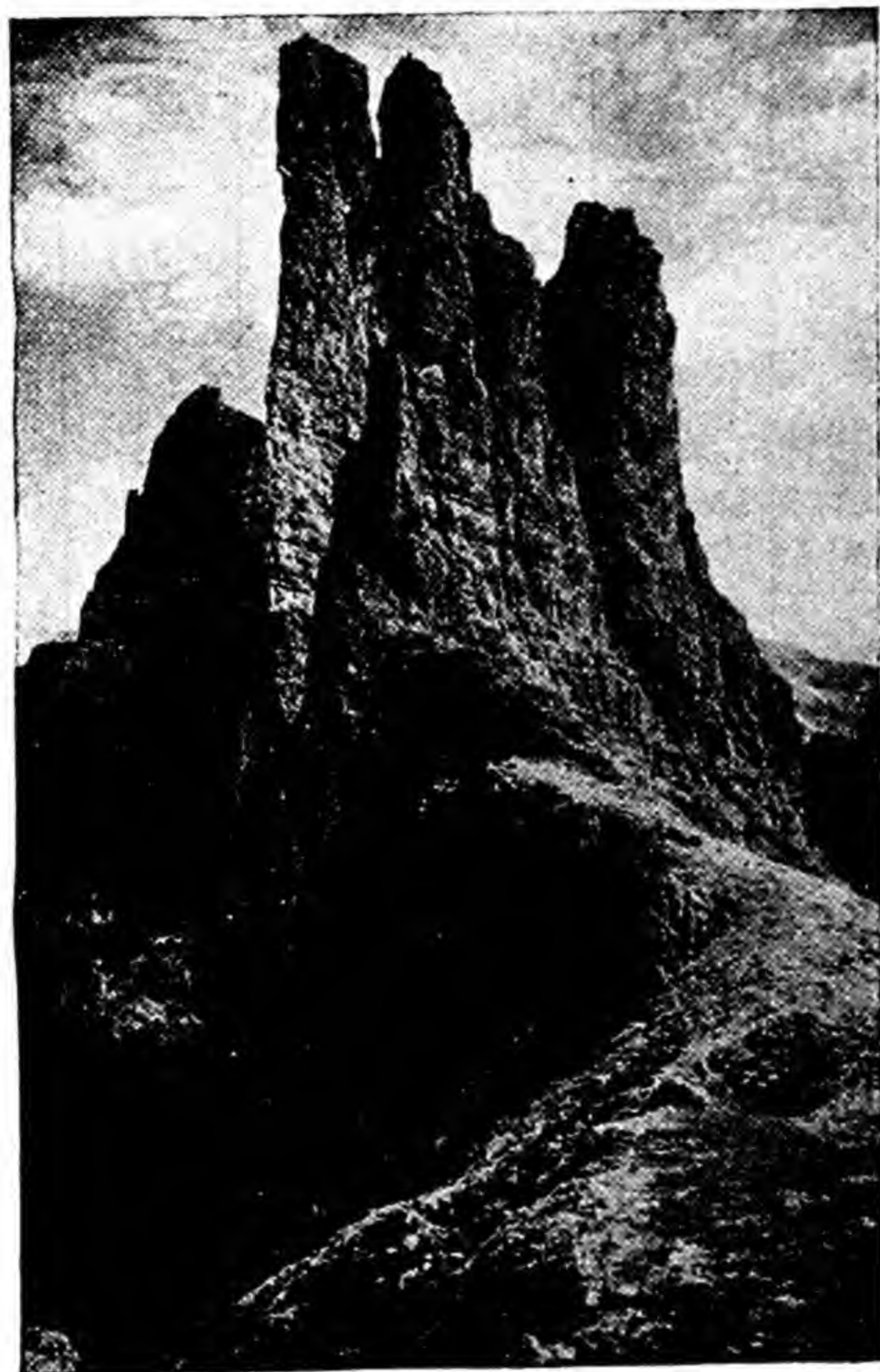


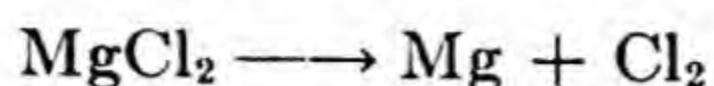
Fig. 153. Mountains of dolomite in northern Italy.

nallite, $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ is another important mineral containing magnesium.

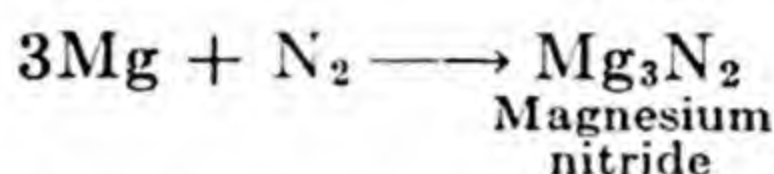
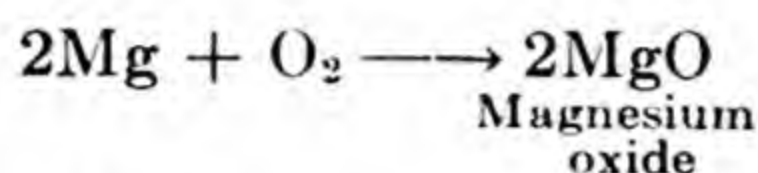
Magnesium sulfate, a colorless crystalline salt, is used in medicine as a laxative. In 1695 the springs of Epsom, England, were found to have medicinal value. About one hundred years later the bitter salt present in the water was identified as magnesium sulfate (Epsom salts, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$).

Preparation. The pure metal is prepared by the electrolysis of its salts. The mineral carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot \text{H}_2\text{O}$, is usually the salt employed for this purpose. We may represent the result

of the electrolysis by the equation



Properties. Magnesium is a silvery-white metal. It is one of the lightest of the elements, being only two-thirds as heavy as aluminum. Magnesium reacts with water slowly at 100°C., giving hydrogen and magnesium hydroxide, but at room temperature it is not appreciably affected by water. The metal burns in air with a brilliant white light, combining with oxygen and with nitrogen:



When magnesium is heated to its ignition point it burns brightly in an atmosphere of carbon dioxide, taking oxygen from the carbon atom:

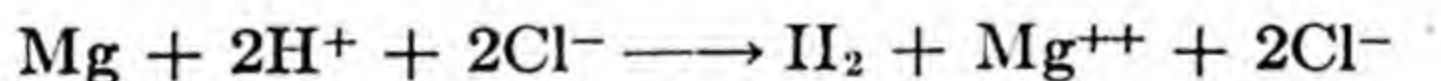


It burns also with great rapidity under water:



The burning of magnesium results in the release of more heat than is required to decompose the water. Most of the hydrogen released in this reaction burns in the surrounding air, re-forming water.

Magnesium reacts rapidly with dilute acids, liberating hydrogen and forming the corresponding magnesium salt:



Uses of magnesium. Magnesium has many important uses. When dissolved in other metals it forms light, strong alloys which are used in the manufacture of automobiles and airplanes. One of these, magnalium, is composed of magnesium and aluminum. Other alloys having slightly different qualities are made of magnesium, aluminum, manganese, and cadmium, and still others contain magnesium, aluminum, zinc, and tin.

Because of the brilliancy of the flame produced when magnesium burns, it finds use in flashlight powders, in fireworks, and in flares which are released by airplanes. The metal is used also to remove the last trace of oxygen and nitrogen from radio vacuum tubes. Large amounts of magnesium have been used in making incendiary bombs.

Several of the compounds of magnesium have important uses. The hydroxide and sulfate of magnesium are used medicinally. The hydroxide, suspended in water, is sold as milk of magnesia, and the sulfate as Epsom salts. Magnesium oxide, or magnesia, as it is usually called, is made into the form of bricks for lining furnaces because of its very high melting point. Mixed with asbestos, it is used as a covering for steam and hot water pipes. Magnesia is used also as an adulterant in paints, as an absorbent for nitroglycerine in the manufacture of dynamite, and in the vulcanization of rubber. Large quantities of magnesium carbonate are used in the manufacture of toothpastes and powders, and for silver polish.

The presence of a small amount of magnesium chloride in our table salt causes the salt to become moist in damp weather and to clog the openings in the salt cellars. Magnesium chloride is deliquescent; sodium chloride is not. Talc is the basis of talcum powder, and mica is used extensively as an insulator in electrical work; both are forms of magnesium silicate.

Questions and Exercises

1. Write an equation for the reaction of magnesium with hot water.
2. Enumerate three uses of magnesium.
3. Write an equation for the process for making magnesium from its fused salt.
4. Write the equation for the reaction between magnesium and dilute sulfuric acid.
5. Calculate the percentage composition of the mineral carnallite, which has the formula $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.
6. What is the percentage of magnesium in Epsom salts?
7. Why is magnesium a valuable constituent of alloys?
8. How many liters of hydrogen, measured under standard conditions, can be made by the action of an excess of hydrochloric acid on 48 g. of magnesium?

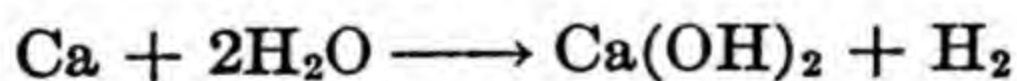
PART 2

Calcium and Its Compounds

Occurrence. Calcium occurs abundantly in the earth's crust but only in combination with other elements. The commonest naturally occurring compound of calcium is the carbonate. Other important minerals are gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, fluor spar, CaF_2 , and apatite, $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$. Calcium occurs also in certain silicates, such as asbestos, and as phosphate rock, $\text{Ca}_3(\text{PO}_4)_2$. Sea water contains compounds of calcium in solution. These compounds are absorbed by sea animals and are converted into the calcium carbonate found in their shells.

Preparation. Metallic calcium is prepared by the electrolysis of molten calcium chloride. A graphite crucible containing the fused salt forms the positive electrode, and an iron bar is used for the negative electrode. The end of the bar is immersed in the molten chloride, and as calcium deposits on the electrode it is slowly drawn up from the fused mass by a screw mechanism. The end of the iron bar is soon above the liquid, and an irregular stick of metallic calcium is then acting as the electrode. Occasionally the calcium is removed and the iron bar is lowered into the molten mass.

Properties. Calcium is a white metal, much harder than silver and slightly lighter than aluminum. It reacts with water to form calcium hydroxide and hydrogen:



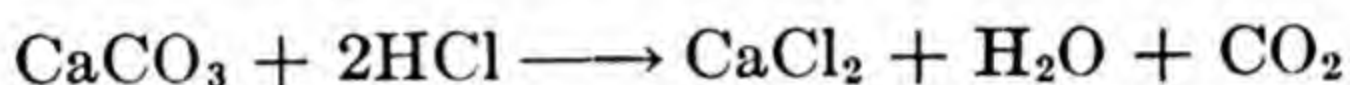
The same reaction occurs when the metal is exposed to moist air and the surface of the metal becomes coated with calcium hydroxide. When heated, the metal reacts with all gases except those of the helium group. With hydrogen, nitrogen, and oxygen it forms calcium hydride, CaH_2 ; calcium nitride, Ca_3N_2 ; and calcium oxide, CaO , respectively. Calcium reacts with dilute acids, liberating hydrogen.

Compounds of Calcium

Calcium carbonate. A common compound of calcium is the carbonate, CaCO_3 , which is found in several different forms.

Limestone occurs in enormous deposits in all countries, and chalk is found in many places. These are forms of impure calcium carbonate derived from shells of various kinds of sea animals. In some places the floor of the ocean is covered with vast deposits of shells. When subjected to pressure, during long geological periods, the shells are converted into marble, limestone, or chalk. Marble is a crystalline form of calcium carbonate. In addition to the impure varieties of calcium carbonate, there are two crystalline forms of the pure compound found in nature. They are known as *calcite* and *aragonite*. These compounds crystallize in different forms, for the atoms composing the crystals are not arranged in the same way in the two minerals.

Calcium carbonate is insoluble in water, but in acids it dissolves readily, evolving carbon dioxide:

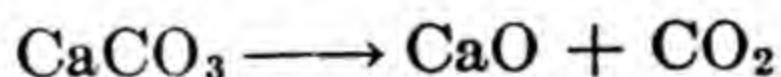


Calcium carbonate may be precipitated from a solution of any soluble calcium salt by the addition of a solution containing a large amount of carbonate ion:

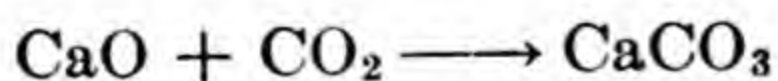


Precipitated calcium carbonate is used in the manufacture of toothpaste and silver polish. Calcium carbonate in the form of limestone is used extensively in the manufacture of cement, lime, and glass, and in the smelting of ores. It is valuable also as a building stone.

Calcium oxide. When calcium carbonate is heated to a high temperature, it decomposes into carbon dioxide gas and a white solid known as calcium oxide or lime:



If, on the other hand, carbon dioxide is passed over *cold* calcium oxide, the reverse reaction takes place. Under these conditions carbon dioxide and calcium oxide combine to form calcium carbonate:

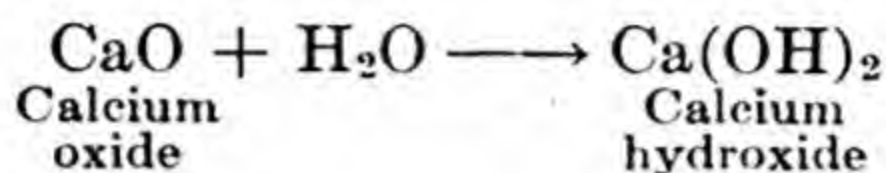


Calcium oxide or lime is manufactured by heating limestone, marble, or shells. In modern plants a rotary kiln is used. Limestone is run in at the upper end of the slightly inclined rotating kiln, and fuel is introduced with an air blast in the lower end. The limestone gradually rolls down into the hotter end of the kiln and is finally ejected as calcium oxide or lime.

Pure calcium oxide is a white, noncrystalline solid. When heated to a high temperature by an oxyhydrogen or oxyacetylene

torch, a lump of lime becomes incandescent, producing a brilliant white light. It was formerly used to produce intense light, as for example, a theater spotlight. The origin of the phrase "in the limelight" dates back to the period when incandescent lime provided the best-known intense light. Calcium oxide is also called unslaked lime, quicklime, or burnt lime.

Calcium hydroxide. Calcium oxide reacts with water to form calcium hydroxide:

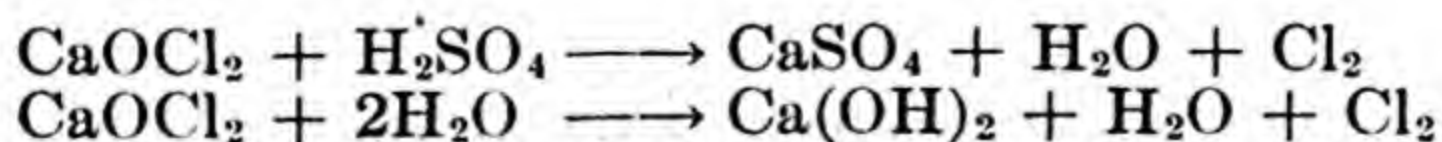


When calcium oxide is allowed to stand exposed to the air for a period of time, it combines with both the carbon dioxide and water vapor in the air. It then contains a mixture of calcium carbonate and calcium hydroxide. Lime treated in this way is often called *air-slaked* lime. Calcium hydroxide is slightly soluble in water, and the solution is known as limewater. When calcium hydroxide is suspended in water (that is, when more lime is added than will dissolve), it forms a mixture resembling milk in appearance, and the mixture is known as *milk of lime*. If allowed to stand, the undissolved calcium hydroxide in milk of lime settles out, and the solution above it is limewater. When limewater is exposed to the air, it absorbs carbon dioxide and forms a covering film of insoluble calcium carbonate:



The same reaction takes place also when solid calcium hydroxide is exposed to air.

Calcium hydroxide absorbs chlorine, forming *chloride of lime*, CaOCl_2 or $\text{Ca} \begin{array}{l} \text{OCl} \\ \text{Cl} \end{array}$. This compound is known also as *bleaching powder*. It reacts rapidly with any acid, or slowly with water, liberating chlorine:

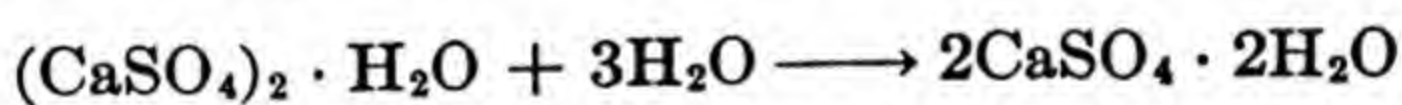


Mortar. This is a paste made from slaked lime, sand, and water. It sets or hardens as it loses water by evaporation. The calcium hydroxide in the dried mortar then slowly reacts with carbon dioxide of the air, forming a superficial layer of calcium carbonate. This layer of calcium carbonate does not become very thick, for its formation prevents the carbon dioxide of the air from reaching the calcium hydroxide beneath it. The ancient

Romans used mortar for their walls, and this mortar, after 2000 years of exposure, is covered with a fairly thick layer of calcium carbonate, but calcium hydroxide is found in the interior.

Calcium hydroxide is used principally in making mortar, in the manufacture of chloride of lime, in softening water, in the tanning industries to remove hair from hides, in the manufacture of ammonia from ammonium salts, in the manufacture of sodium hydroxide, in the purification of sugar and illuminating gas, and in neutralizing acidic soils.

Calcium sulfate and plaster of Paris. Enormous deposits of gypsum are found in nature. The formula for gypsum is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Two molecules of water are held by every molecule of calcium sulfate in this crystalline compound, and when it is heated to a high temperature all the water in gypsum is driven out and anhydrous calcium sulfate, CaSO_4 , is formed. If, however, gypsum is heated to about 175°C ., it loses only three-quarters of its water, and *plaster of Paris* is formed. This has the formula $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$. In this compound one molecule of water is associated with every two molecules of CaSO_4 . When plaster of Paris is mixed with water, it takes up enough water to form gypsum. A thick paste of plaster of Paris and water *sets*, or becomes hard, through the formation of minute crystals of gypsum:



The paste expands slightly on setting and fills a mold perfectly. It is, therefore, very valuable in making plaster casts. Gypsum is sparingly soluble in water and it dissolves very slowly.

Calcium chloride. The chloride of calcium, CaCl_2 , is a deliquescent salt. It absorbs water from the atmosphere until it actually dissolves. It is used in the laboratory for drying liquids and gases. A solution of calcium chloride is valuable for road sprinkling, for the salt prevents the complete evaporation of the water and the road remains moist and dustless. All volatile salts of calcium impart a brick-red color to a flame.

Questions and Exercises

1. Name three common forms of calcium carbonate.
2. Is calcium carbonate soluble (a) in water, (b) in hydrochloric acid, (c) in nitric acid, (d) in carbonic acid?
3. How is plaster of Paris made and how is it used?
4. How is metallic calcium obtained from calcium chloride?
5. What volume of carbon dioxide measured under standard conditions can be obtained from 200 g. of calcium carbonate?

6. What weight of lime can be made from 10 tons of limestone? Assume that limestone is 90 per cent CaCO_3 .

7. If slaked lime is heated, it may be reconverted into quicklime. Write the equation for the reaction taking place when this occurs.

8. Beginning with limestone as the crude material, how would you prepare precipitated calcium carbonate in the most economical way? Write an equation for each step of the process.

9. A certain plaster cast weighed 15 lb. What weight of dry plaster of Paris was necessary to make this cast?

10. Carbon dioxide in moist air reacts with chloride of lime, CaOCl_2 , liberating chlorine. Write an equation for the reaction.

11. Write equations for the reactions that take place when lime is air-slaked.

12. Why would you not expect to find calcium free in nature?

13. Would you expect to find deposits of calcium oxide or of calcium hydroxide in nature? Give reasons for your answers.

14. Write equations for the following reactions:

(a) Calcium + sulfuric acid (dilute) \longrightarrow

(b) Calcium hydroxide + sulfuric acid \longrightarrow

(c) Calcium oxide + hydrochloric acid \longrightarrow

(d) Calcium carbonate + hydrochloric acid \longrightarrow

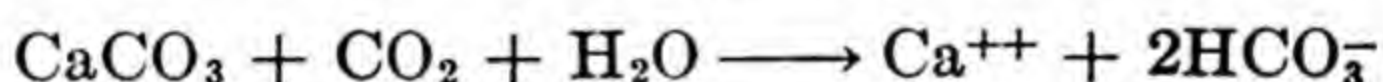
PART 3

Hard Water and Its Softening

Formation of hard waters. We have learned that all natural waters found on the surface of the earth contain dissolved substances. Some of these substances are beneficial, but others must be removed before the water can be used in our everyday life.

When water passes over or through regions where the soil and rocks comprise compounds of calcium and magnesium, small amounts of these substances dissolve in the water, forming so-called "hard water."

Temporary hardness. Limestone, CaCO_3 , is very slightly soluble in pure water. Surface water, however, is usually saturated with carbon dioxide formed by the decay of animal and vegetable matter in the soil. When this charged water passes over limestone, the same reaction takes place that we observed when we passed an excess of carbon dioxide into limewater:



The calcium bicarbonate dissolves readily in water.

When soap is added to water containing calcium ions, a sticky, white precipitate is formed. This is an insoluble salt formed between the calcium ions and the soap. This salt adheres to anything that is immersed in the water and prevents the soap from forming a lather. Washing in hard water is therefore a very unsatisfactory process.

When water containing calcium bicarbonate is heated, the insoluble calcium carbonate is precipitated, and carbon dioxide passes off into the air. This process removes the calcium salt from the water; hence a solution of calcium bicarbonate is said to be temporarily hard water. We have all seen the boiler scale that deposits in a teakettle. This is mainly calcium carbonate. It is a very poor conductor of heat, and when there is a heavy deposit it may cause the metal in the bottom of the kettle to melt, ruining the utensil for further use. The same scale settles in the tubes of the boilers in steam engines, making the boilers inefficient and causing tremendous losses yearly. An automobile radiator

gradually becomes clogged with the same deposit, causing the engine to overheat because of the reduced surface and poor conductivity of the radiator.

Permanent hardness. When water contains calcium sulfate and magnesium sulfate, it is said to be permanently hard, since these salts are not removed by heating the water.

Water softening. Temporary hardness is often overcome by heating the water, but this method cannot be applied on a large scale because of the expense for fuel. Chemical softeners are



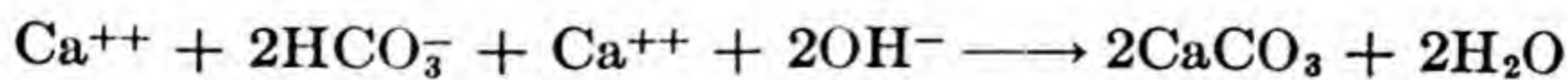
Courtesy, Permutit Co.

Fig. 154. Boiler scale.

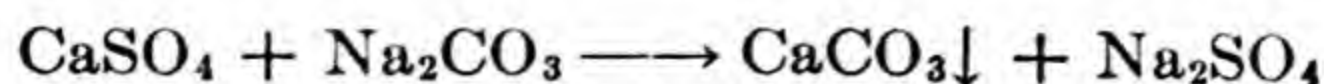
generally employed. Sometimes ammonia is added to the water for this purpose. The reaction that takes place is shown in the following equation:



The calcium ions are removed from the solution as insoluble calcium carbonate, while the harmless ammonium ion remains in solution. Another method for accomplishing the same result depends upon the use of calcium hydroxide. The following reaction takes place:



Permanently hard waters are softened by the use of sodium carbonate:



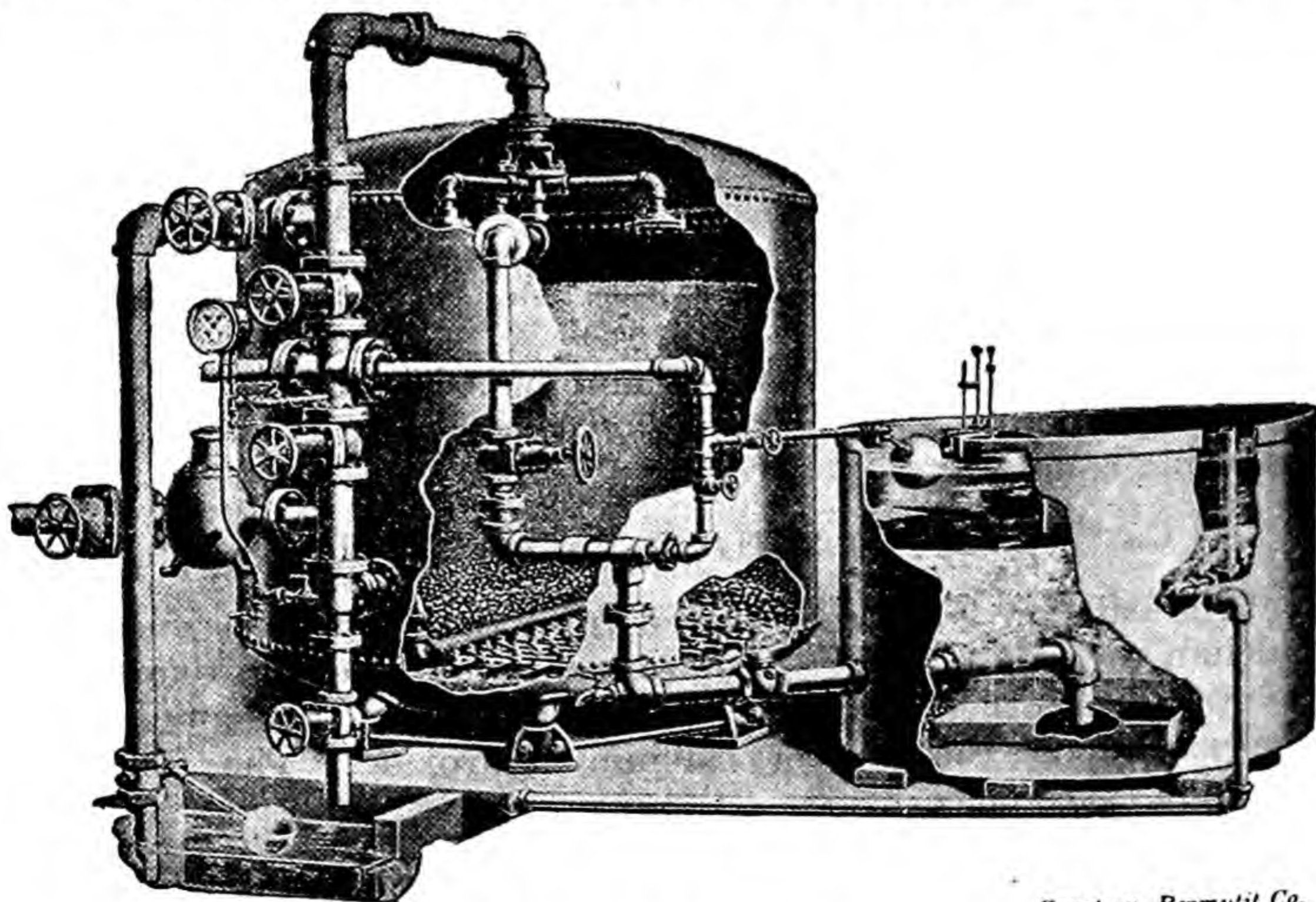
The sodium ions and sulfate ions left in the solution do not interfere with the action of soap and do not deposit in utensils or boilers.



Courtesy, Permutit Co.

Fig. 155. Zeolite used in the Permutit process. One portion of the mass magnified.

Another common method of softening water is known as the *zeolite* or *Permutit* process. Zeolite is an insoluble sodium aluminum silicate. The composition of zeolite varies somewhat,

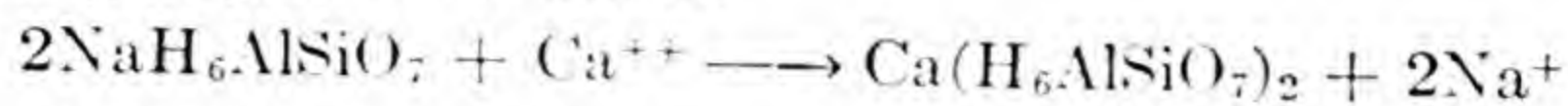


Courtesy, Permutit Co.

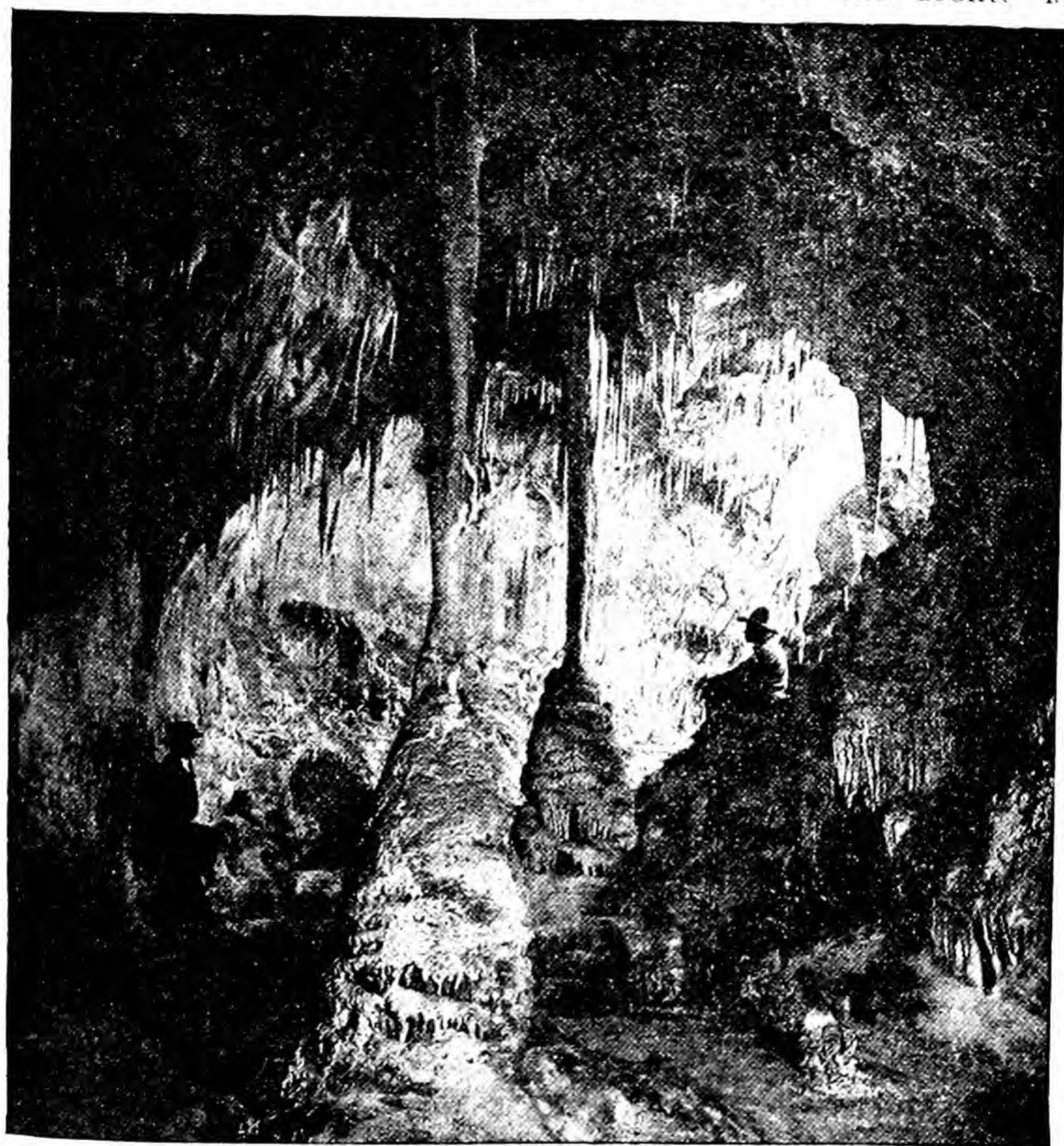
Fig. 156. Permutit water softening apparatus.

but its approximate formula is $\text{NaH}_6\text{AlSiO}_7$. The sodium of the zeolite is replaceable by calcium, and if hard water comes in contact

with zeolite the insoluble calcium salt, $\text{Ca}(\text{H}_6\text{AlSiO}_7)_2$, is formed, sodium ions going into solution:



This process is carried out by allowing the hard water to flow through tanks containing zeolite. When the zeolite is



Courtesy, El Paso Chamber of Commerce

Fig. 157. Stalactites and stalagmites. Carlsbad Caverns.

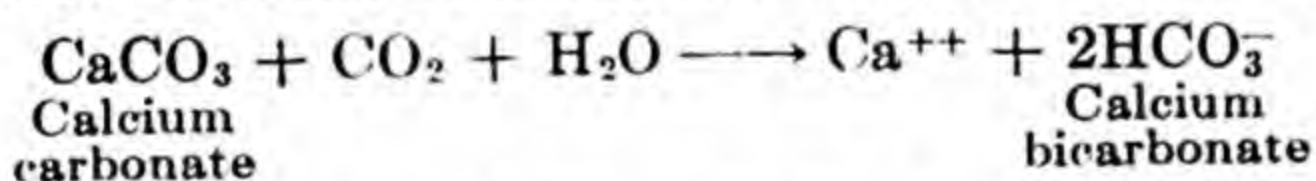
exhausted, the process may be reversed and the zeolite regenerated by treating the calcium salt with a concentrated solution of sodium chloride. The regenerating process, which is accomplished in a few hours, is represented by the reverse of the last equation. Zeolites occur naturally, and they may be manufactured artificially.

Other processes of water softening are known, but the chemical reactions involved are beyond the scope of this course. Special soaps are made for use in ocean water. Several compounds, sold under various trade names, render hard water suitable for laundry purposes without precipitating the calcium salts. Sodium hexametaphosphate, $\text{Na}_6\text{P}_6\text{O}_{18}$, and sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$, are such compounds. Another type of softener is described on page 483.

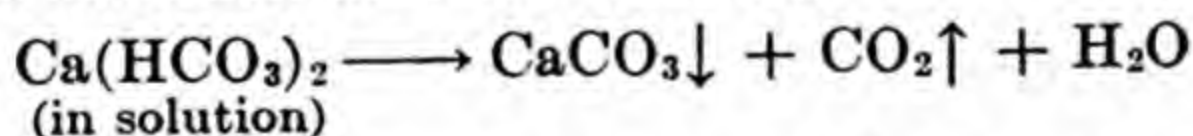
Formation of limestone caves. In many limestone regions underground caverns have been formed through the gradual dissolving of the stone by water containing carbonic acid. Water dripping from the roof of such a cave loses part of its carbon dioxide, and at the same time calcium carbonate is formed as an insoluble residue on the roof of the cave. In time the roof of the cavern becomes studded with *stalactites* of crystalline calcium carbonate. Evaporation of water that drips from the stalactites is accompanied by deposition of calcium carbonate on the floor of the cave. These deposits are called *stalagmites*. Caves formed in this way are found in many places. The Carlsbad Caverns in New Mexico and the Mammoth Cave in Kentucky are well-known examples.

Questions and Exercises

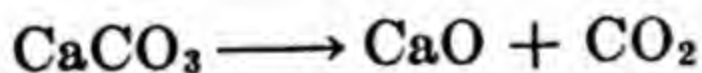
1. Under what condition does the following reaction occur in nature?



2. Is calcium bicarbonate soluble in water?
3. Under what condition does the following reaction occur?



4. State the conditions necessary to cause the change represented by the equation



5. Is the equation given in Exercise 4 reversible? If so, specify the conditions necessary to cause it to go from right to left.

6. What is meant by the term "temporary hardness" as applied to water?

7. Show how water may be "softened" if the hardness is due to (a) $\text{Ca}(\text{HCO}_3)_2$; (b) CaSO_4 .

8. What compounds dissolved in water cause "permanent hardness"?

9. Explain the formation of a layer of solid matter in a teakettle.

10. Explain the formation of stalactites and stalagmites.

11. A manufacturing plant has a tank for softening water which holds 50,000 gal. of water. If each gallon of water contains 0.25 g. of calcium sulfate, how much sodium carbonate is necessary to soften the water? If this amount of water is not softened, how much boiler scale in the form of calcium sulfate is it capable of producing?

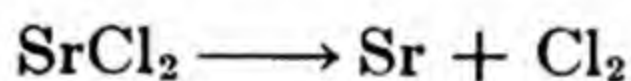
PART 4

Strontium, Barium, and Radium

Strontium

Occurrence. Strontium, like magnesium and calcium, is never found free in nature. Its principal ores are strontianite, SrCO_3 , and celestite, SrSO_4 . The latter is often found in caves in the form of beautiful crystals with a bluish tinge. Such a cave located near Lake Erie is especially famous. Another large deposit of strontium sulfate has been discovered in Arizona.

Preparation. Strontium is prepared exactly as are the other members of this group—by the electrolysis of the melted chloride:



Properties and uses. The properties of strontium are similar to those of calcium. Since in uniting with other elements it yields two valence electrons, the strontium atom has a charge of 2 in all its compounds. Strontium salts impart a red color to a flame. This color serves as a test for the strontium ion.

The most important use of strontium is for the production of a red color in fireworks, "red fire" for railway danger signals, and military flares. Strontium nitrate, $\text{Sr}(\text{NO}_3)_2$, is usually used for this purpose.

Barium

Occurrence. Barium is found in many places in the form of the ore barite, or heavy spar (BaSO_4). Barium carbonate, BaCO_3 , also is found in several localities.

Preparation and properties. The metal is prepared by the electrolysis of its fused chloride. It has a silvery color, is soft, and can be hammered into sheets. It burns spontaneously when exposed to moist air.

Compounds of barium and their uses. Barium sulfate is one of the most important salts of barium. It is highly insoluble in water, and insoluble also in acids and bases. It is used in the production of the white pigment *lithopone*. To produce it, barium

sulfate is heated with carbon and converted into the sulfide BaS:

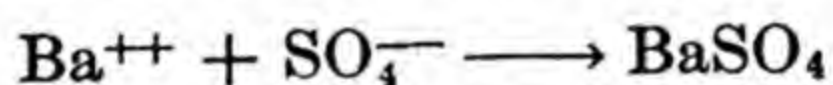


Barium sulfide is soluble, and is added to a solution of zinc sulfate, ZnSO_4 , which also is soluble. The barium and zinc atoms exchange places, forming two insoluble compounds, barium sulfate, BaSO_4 , and zinc sulfide, ZnS , both of which are white:



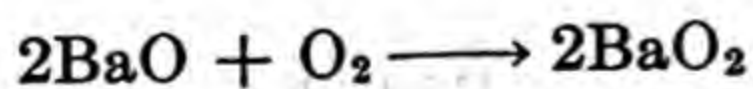
Barium sulfate is used also as a filler for glazed paper. It is sometimes used to impregnate matches, giving them the "no afterglow" property. A suspension of barium sulfate in water or milk is administered when an X-ray examination is made of the digestive tract. The heavy barium atoms stop the passage of X rays through the otherwise transparent organs, causing them to produce a shadow similar to that made by the bones.

The insolubility of barium sulfate is the basis for an analytical test for barium and also for sulfate ions. Sulfuric acid, or any soluble sulfate, is added to a solution to be tested for barium ions. A white precipitate insoluble in acids is formed if barium is present. A soluble barium salt, such as barium chloride, is used to test for sulfate ion. In either case the ionic equation is:

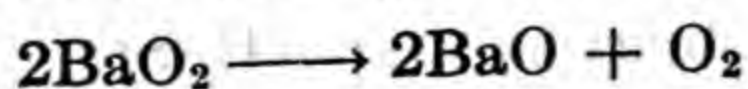


Barium salts color the Bunsen flame a bright green. This color serves as a test for the barium ion. Because of this color, barium salts find use in fireworks and in the manufacture of "green fire."

Barium oxide, obtained by heating barium carbonate or barium nitrate, is another compound that has important uses. When barium oxide is heated in the presence of air, it forms barium peroxide:



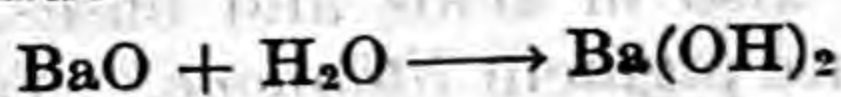
At a higher temperature barium peroxide gives up oxygen:



One method of obtaining pure oxygen from the air (Brin's process) is based upon these reactions. It furnishes pure oxygen at a reasonable cost.

You will recall that barium peroxide is used with sulfuric acid in the preparation of hydrogen peroxide.

When barium oxide is dissolved in water, it forms the strong base, barium hydroxide:



Radium

The story of the discovery of radium is one of the most interesting chapters in the history of science. Soon after the discovery of X rays, Becquerel, a French chemist, observed that a uranium salt placed near a photographic plate affected the plate as X rays would. Rays given off by the uranium salt could penetrate the cardboard cover of a box of plates and produce the same result that exposure to light would produce.

Monsieur and Madame Curie, co-workers of Becquerel, discovered that pitchblende, which corresponds approximately to the formula U_3O_8 and is the principal ore of uranium, was more active—that is, gave off more rays—than freshly prepared uranium oxide, U_3O_8 . They concluded that the ore contained some substance more active than uranium. They undertook to separate this active substance from the pitchblende and succeeded in obtaining an impure product that was much more active than the original pitchblende. They tried to purify this product, but each step in the purification left them with a smaller quantity of the radioactive material, and complete purification seemed to be impossible. Finally they worked with many tons of pitchblende, and from this vast supply they succeeded in obtaining a small fraction of a gram of the bromide of a new element. They called the new element *radium*.

Occurrence. Radium is obtained from uranium ores, which always contain a small amount of radium. The first deposit of uranium ore, called *pitchblende*, was found in Bohemia. Later, small deposits of radium ores were found in Portugal. The first nation to develop a large-scale industry for the production of radium was the United States. The metal was obtained from carnotite ores found in the Rocky Mountains. Richer deposits were discovered later in the Belgian Congo and in the Great Bear Lake region of Canada.

Extraction from its ores. Radium is obtained from its ores by precipitating it as radium sulfate. The sulfate is reduced to the sulfide by heating with carbon, and the radium sulfide is then dissolved in hydrochloric acid to convert it into the chloride:



Pure radium chloride is obtained by recrystallization of the impure salt. The free metal is obtained by electrolysis of the chloride.

Properties. Radium is similar to calcium and barium in both physical and chemical properties. It tarnishes in the air, and reacts with water at moderate speed, liberating hydrogen.

It forms an insoluble carbonate and sulfate, similar to those of barium. Its hydroxide is a moderately strong base.

Radium possesses an enormous store of internal energy. When it is placed near zinc sulfide, fluorspar, or diamonds, these become brilliantly luminescent. It produces severe burns on the flesh and coagulates proteins. It transforms oxygen into ozone. It gradually disintegrates and, through a chain of radioactive intermediate products, it is ultimately converted into lead.

Uses. Radium is used in the manufacture of luminous paint, which is often seen on the dials of clocks and watches. The instruments on airplanes equipped for night flying are coated with paint containing a trace of radium bromide.

Radium has some therapeutic powers. Its rays seem to have a greater effect on unhealthy tissue than on normal tissue, and it is used extensively in the treatment of cancer.

THE ALKALINE EARTH METALS

	Flame color	Solubility of salts		Strength of base
		Chloride	Sulfate	
Magnesium.....	—	Most soluble	Most soluble	Strong
Calcium.....	Brick red			Strong
Strontium.....	Deep red			Strong
Barium.....	Green			Strong
Radium.....	—	Least soluble	Least soluble	Strong

Questions and Exercises

1. Name the elements that constitute the second main group of the periodic system.

2. In what respect do the alkaline earth metals resemble the alkali metals? How do they differ?

3. How would you distinguish between (a) barium carbonate and barium sulfate, (b) barium chloride and strontium chloride, (c) calcium sulfate and barium carbonate?

4. The solubilities of the chlorides and nitrates of calcium, strontium, and barium decrease in the order in which the elements are named. Predict the relative solubilities of magnesium chloride and radium chloride.

5. The barium ion, Ba^{++} , is poisonous, but barium sulfate is not poisonous. Explain.

6. Barium sulfate is given internally when X-ray photographs are made of the alimentary canal. Barium carbonate and barium sulfate are about equally insoluble in water. Patients have been killed by attendants who administered barium carbonate instead of barium sulfate. Explain.

7. One solution contains carbonate ions and another contains sulfate ions. When barium chloride is added, a white precipitate is formed in each case. How could you determine which precipitate is barium carbonate and which is barium sulfate?

8. Write an equation for the preparation of each of the alkaline earth metals.

9. Write an equation for the preparation of barium oxide from the carbonate.

10. What reaction would you expect to take place when water containing carbon dioxide in solution passes over barium carbonate? Write the equation.

11. Would you expect hydrolysis to take place when the following salts are dissolved in water: (a) MgSO_4 ; (b) CaCl_2 ; (c) $\text{Sr}(\text{NO}_3)_2$; (d) BaCl_2 ; (e) RaCl_2 ?

UNIT XII

Group III of the Periodic Table: Boron and Aluminum

PART 1

Boron

Group III of the Periodic Table is composed of the elements aluminum, boron, scandium, yttrium, lanthanum, and actinium. The subgroup contains the elements gallium, indium, and thallium. Boron and aluminum are the most important members of this group, and are the only ones which will be considered in any detail.

PHYSICAL PROPERTIES OF BORON AND ALUMINUM

	Boron	Aluminum
Atomic weight.....	10.82	26.97
Atomic number.....	5	13
Electron structure:		
1st shell.....	2	2
2nd shell.....	3	8
3rd shell.....	—	3
Melting point, °C.....	2300	658
Boiling point, °C.....	2550	1800
Density, grams per cubic centimeter.....	2.4	2.70
Isotopes.....	10, 11	none

Boron

Occurrence. Boron does not exist in the free state in nature, but it does occur as boric acid, H_3BO_3 , and as borates. The deposits of these compounds have resulted from the evaporation of inland seas. In Germany the deposits of boron are principally magnesium borates. In the western United States there exist large deposits of colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$, and some borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$. Boron silicates and aluminates are widely distributed in rocks.

Preparation and properties. Boron is prepared by heating the oxide, B_2O_3 , with powdered magnesium.

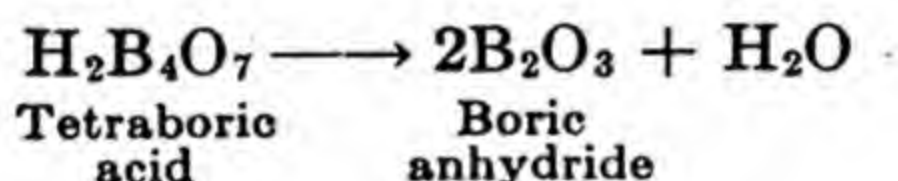


The free element as usually prepared is a dark brown powder. When melted and cooled, the substance is brittle, practically a nonconductor of electricity, and almost as hard as the diamond.

Boron oxidizes slowly in the air at 100°C. and burns at higher temperatures with a green flame. It does not dissolve in acids, but is soluble in fused alkalis, forming borates.

The free element has no practical use. Some of its compounds, especially boric acid and borax, find many uses in everyday life.

Boric acid (H_3BO_3). In some volcanic regions boric acid is found in hot springs and in the steam issuing from the craters of extinct geysers. Hot springs in Tuscany (Italy) are commercial sources of boric acid. The steam containing boric acid is condensed, and the acid is obtained in the solid state by evaporation of the water. Most of the boric acid which we use, however, is made from borax. Boric acid is a weak acid, since, in water solution, it is only slightly dissociated into its ions. The solid exists in white, slippery, crystalline scales. It is a mild antiseptic, and a 2 per cent solution of the acid is used as an eyewash. When boric acid is heated, it loses water, yielding tetraboric acid, $\text{H}_2\text{B}_4\text{O}_7$, and finally boric anhydride, B_2O_3 :



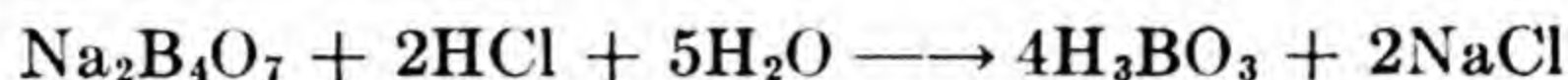
Boric acid may be recognized by the green tint which it gives to the flame when its solution in alcohol is burned.

Borax. Sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$, the sodium salt of tetraboric acid, crystallizes from aqueous solution with 10 molecules of water. This hydrated salt, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, is called *borax*. It is made by treating the calcium salt of tetraboric acid, *colemanite*, with sodium carbonate. The calcium carbonate formed is insoluble, and is filtered off from the water solution of borax. Large deposits of calcium tetraborate are found in Death Valley, California, and in Nevada. Many of us have seen pictures of the twenty-mule teams which were formerly used for transporting the borax across the desert to civilization.

Borax is a white, crystalline salt. Because of the smoothness of these crystals, borax has been used as a substitute for snow on slides for ski practice. Borax is a salt of a very weak acid and a strong base. Consequently, a solution of borax has an alkaline reaction, owing to hydrolysis of the salt. This property makes

borax useful as a cleaning agent, and as such it is incorporated in some soaps.

A strong acid such as hydrochloric acid acts upon borax, precipitating boric acid:



Most of the boric acid in use today is made by this method. Borax combines readily with oxides of metals when fused with them, and it is used for this purpose to dissolve the films of iron oxide on pieces of red-hot iron that are to be welded together. It is used also to clean metallic surfaces that are to be soldered.

Borax beads. Another use for borax, which depends upon its ability to dissolve oxides of metals, is found in qualitative analysis. Borax is heated in a flame on a small loop of platinum wire until it melts, forming a clear glassy bead that fills the loop. The bead is then remelted with a trace of the substance to be analyzed. If cobalt is present, the bead acquires a beautiful blue color. Chromium imparts a green color to the borax bead, and manganese gives it a violet color.

Questions and Exercises

1. Name two compounds of boron.
2. State two uses of borax.
3. Calculate the weight of magnesium required to reduce 5 lb. of boron oxide.
4. Write a balanced equation representing the formation of boric anhydride from boric acid.
5. Calculate the per cent of water in borax.
6. How could you distinguish between cobalt chloride and manganese chloride?
7. How could you prove that boric acid is an exceedingly weak acid?
8. Write the equation for the hydrolysis of borax.

PART 2

Aluminum

Occurrence. Next to oxygen and silicon, aluminum is the most abundant of the elements. It is a very active metal and never found in the free state. Its compounds are plentiful and widely distributed. Most of the common rocks and clays are complex aluminum silicates. Micas and feldspars are common examples. Some of the precious stones are aluminum compounds. Rubies and sapphires are crystalline aluminum oxide, Al_2O_3 , containing small amounts of other substances, and garnet is a silicate of aluminum and calcium. Turquoise is a form of aluminum phosphate. Bauxite or hydrated aluminum oxide is represented approximately by the formula $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, but it usually contains a little iron oxide. Cryolite is a double fluoride of sodium and aluminum. It has the formula Na_3AlF_6 . These minerals are commonly used in the preparation of aluminum. Emery, a crude aluminum oxide, is used extensively as an abrasive in the form of grinding wheels, emery cloth, and powder. Alundum, which is aluminum oxide that has been fused in an electric furnace, is now considered superior to native emery as an abrasive.

Preparation. Although aluminum makes up almost one-twelfth of the earth's crust, it is locked so securely in combination with other substances that for many years after its discovery it could not be obtained pure at a reasonable cost. Aluminum was first obtained about the middle of the last century by reducing the chloride at a high temperature with sodium. The cost of aluminum secured by this process was in the neighborhood of \$8 a pound. Scientists early recognized the great commercial value of aluminum, because of its light weight and other excellent metallic properties, and they tried in every conceivable manner to perfect a method by which it might be obtained easily.

It remained for a young man, Charles Martin Hall, 'teen-aged son of an Ohio minister, to perfect the process which is used today, and which has reduced the price of the metal to fifteen cents a pound. Hall, working in a crude laboratory in his father's woodshed, found that molten cryolite would dissolve aluminum oxide,

and that the resulting solution would conduct the electric current. Hall passed an electric current through the molten mixture and decomposed the aluminum oxide into aluminum and oxygen. A Frenchman, Hérault, working entirely independently of Hall, discovered the process at about the same time.

In the Hall process, the electrolysis is carried out in a huge iron pot having a carbon lining. The pot acts as the cathode, or negative electrode. The positive electrode, or anode, consists of a number of graphite rods which extend down into the pot. To start the operation, the graphite rods are lowered until they touch the cathode, causing an electric arc. Powdered cryolite is then put into the pot, and becomes melted due to the heat of the arc. When sufficient liquid has been produced, aluminum oxide is dissolved in the cryolite, and the graphite electrodes are drawn away from the cathode. Oxygen is liberated at the anode, while aluminum forms at the bottom of the cell. It remains in the liquid state, since the temperature of the solution is maintained at about 1000°C. From time to time the molten metal is drawn off from the bottom of the cell.

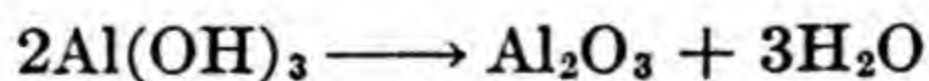
Ordinary commercial aluminum is about 99.0 to 99.5 per cent pure. Since it is very difficult to purify the metal, the aluminum oxide used in the process is usually purified before it is dissolved in the cryolite. The oxide is first dissolved in sodium hydroxide to form sodium aluminate. Contaminating compounds do not dissolve in the sodium hydroxide:



The filtered solution of sodium aluminate is allowed to stand in contact with crystallized aluminum hydroxide. Hydrolysis takes place according to the following reaction, and aluminum hydroxide is precipitated:



The precipitated aluminum hydroxide is then dried and heated, yielding pure Al_2O_3 .



Many attempts have been made to convert clay into aluminum oxide, but no commercial process has as yet been developed.

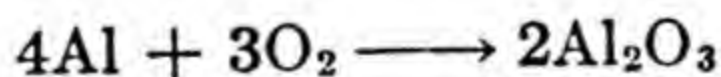
Properties and uses. Aluminum is a silvery-white metal which is only 2.6 times as dense as water. It ranks next to silver, copper, and gold in its ability to conduct heat and electricity. It can be hammered, drawn, and rolled into desired forms, but the pure metal cannot be turned into shape on a lathe, for it clings to

the tools. Magnalium, an alloy which is 90–95 per cent aluminum and 10–5 per cent magnesium, can be worked on a lathe. The lightness and high tensile strength of some aluminum alloys give the metal high commercial value for use in the construction of airplanes and other types of machines in which it is important to avoid unnecessary weight. Valuable alloys are made by fusing aluminum with varying quantities of copper. Duralumin contains 4 per cent copper, $\frac{1}{2}$ per cent magnesium, and $\frac{6}{10}$ per cent manganese. Like steel it can be tempered, and in this condition it is as strong as ordinary steel. It is used extensively in aircraft construction.

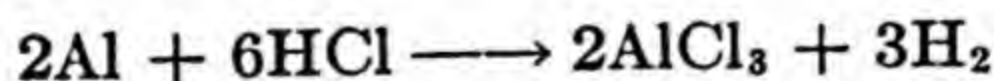
Aluminum is used also for cooking utensils, since it provides effective transmission of heat. It is also used for aluminum boats, paint, foil, electric cable, girders and other structural shapes for bridges, cornices and window frames for buildings, and even for chairs. The modern streamlined railroad train, which depends on its lightness for high speeds, is composed largely of aluminum alloys. Large quantities of aluminum are used for removing the oxygen from iron in steel furnaces. Aluminum takes a high polish, and is highly efficient in reflecting light. Because of these properties it is used as a coating on glass mirrors and reflecting telescopes.

A new aluminum alloy has been developed which has a tensile strength 10 to 25 per cent higher than any other aluminum alloy produced heretofore. The alloy is expected to reduce the weights of planes by at least 10 per cent: 250 pounds in the case of a small plane or up to 3500 pounds for a bomber.

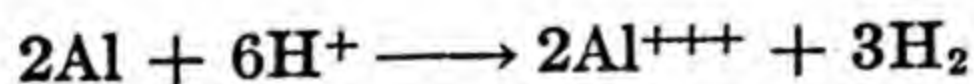
Aluminum burns rapidly when heated in air. Even at ordinary temperatures it oxidizes, but the thin film of oxide first formed clings to the surface and protects the major part of the metal from oxidation.



Aluminum dissolves readily in hydrochloric acid, with evolution of hydrogen:



Or:



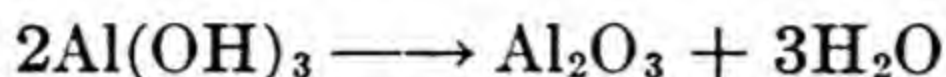
It dissolves also in hot alkalies, forming soluble salts (aluminates) corresponding to the formulas KH_2AlO_3 and KAlO_2 . Hydrogen gas is evolved at the same time.

Aluminum hydroxide. A white gelatinous precipitate is formed when ammonium hydroxide is added to a solution of an

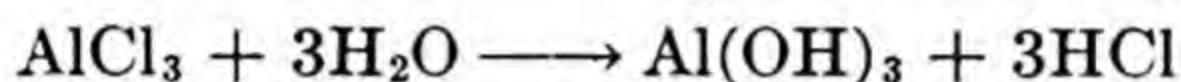
aluminum salt:



When heated, the hydroxide is converted into the oxide, Al_2O_3 :



Aluminum hydroxide is used as a mordant in dyeing cotton fabrics. A mordant is a substance which adheres to textile fibers and also to a dye. Many dyes will not cling to cotton, but they adhere firmly to aluminum oxide or to the hydroxide. The cloth is immersed in a soluble aluminum salt, then steamed. Steam hydrolyzes the salt, leaving the fiber filled with fine particles of aluminum hydroxide:



The acid formed in this reaction is soluble, and it is easily washed out of the cloth. The cloth is then immersed in the dye bath, and the dye adheres to the aluminum hydroxide.

Aluminum oxide. Aluminum has so great a tendency to combine with oxygen that it will take oxygen from many other elements. It is, therefore, a powerful reducing agent. When a mixture of aluminum powder and an oxide of some other element is ignited, a rapid combustion and very high temperature result. Aluminum oxide and the free element are formed. Pure chromium, uranium, manganese, and silicon can be produced in this way:



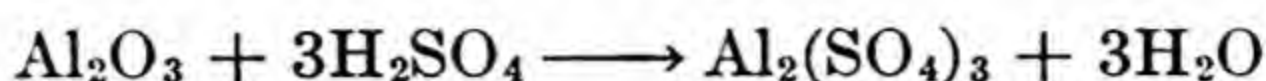
A mixture of aluminum powder and iron oxide is called *thermite*. When the mixture is ignited by means of a piece of magnesium ribbon, aluminum oxide and iron are formed:



A temperature of 3000° to 3500°C . is produced in this way, and the molten iron goes to the bottom of the crucible. This process is used in welding steel rails, large castings, and propeller shafts. The ends to be joined are packed in a mold under the charge of thermite. Molten iron fills the space between the ends, forming a perfect weld.

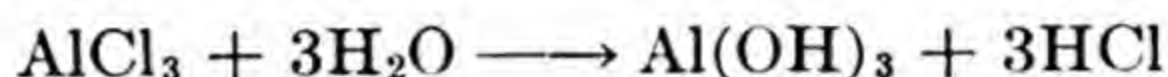
The heat liberated by the reaction between aluminum and iron oxide is tremendous. It has been calculated that when 54 g. of aluminum (2 gram atoms) react with iron oxide, the heat liberated (185,000 cal.) is sufficient to raise the temperature of 185,000 g. of water 1 degree, or it would heat 1,850 g. of water from 0° to 100°C .

Aluminum salts. A white salt, aluminum sulfate, is formed by the action of hot sulfuric acid upon aluminum oxide:



Aluminum sulfate is soluble in water. When it crystallizes, it retains in the crystal 18 molecules of water for every molecule of the salt. The formula for the crystallized salt, therefore, is $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.

Aluminum chloride, AlCl_3 , a white solid, is made by heating metallic aluminum in an atmosphere of chlorine. When exposed to moist air, it reacts with water, forming aluminum hydroxide and hydrochloric acid:



The hydrogen chloride, being volatile, escapes.

Alums. When an aqueous solution containing aluminum sulfate and potassium sulfate is evaporated, the two salts crystallize together. The formula of the double salt formed in this way is usually written $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, or $\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$. There is, however, some evidence that the alum molecule has only half the weight represented by either of these formulas. We should use the formula $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. This double salt is ordinary *alum*. Chrome alum has the formula $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The double formula, however, shows more clearly the nature of the alum as a combination of K_2SO_4 and $\text{Cr}_2(\text{SO}_4)_3$. Other alums can be made by substituting sodium or ammonium for potassium or by substituting iron or chromium for the aluminum. Thus the formula for ammonium chromic alum is written $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Clay. The most useful compound of aluminum is kaolin, a compound having the formula $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_7$. Pure kaolin is used in making porcelain. Ordinary clay is chiefly kaolin, but it contains also feldspar, mica, silica, and other minerals. The ceramic industries depend upon two properties of clay: (1) wet clay forms a plastic mass which can be molded into any desired form; and (2) when the molded material is dried by baking at a high temperature, it becomes hard and retains its molded form. Pottery, earthenware, brick, and tile are among the useful products of ordinary clay.

Questions and Exercises

1. How is aluminum obtained from aluminum oxide?
2. What is an alloy?

3. Name two alloys that contain aluminum, and tell why they are useful.
4. What is thermite and how is it used?
5. What is ordinary alum and how is it made?
6. State several uses for clay.
7. Calculate the percentage composition of sodium alum.
8. Calculate the percentage of chromium in ammonium chromic alum.
9. Write formulas for the nine possible alums.
10. Calculate the weight of a cubic foot of aluminum.
11. What volume of hydrogen measured at standard conditions can be obtained by the action of 9 g. of aluminum on hydrochloric acid?
12. How much iron oxide should be mixed with 5 lb. of aluminum to make thermite?
13. When ammonium hydroxide is added to a solution of ordinary alum, a white precipitate of $\text{Al}(\text{OH})_3$ is formed. When the precipitate is dried and heated, a residue of Al_2O_3 is obtained. Write equations for the two processes and calculate the weight of Al_2O_3 that can be obtained from 35 g. of alum.
14. How many calories of heat would be released in a reaction between 50 g. of aluminum and enough iron oxide to oxidize the aluminum?
15. How many liters of water could be heated from 20° to 90°C . by the heat derived from 50 g. of aluminum and enough iron oxide to convert the aluminum into Al_2O_3 ?

PART 3

Amphoteric Substances

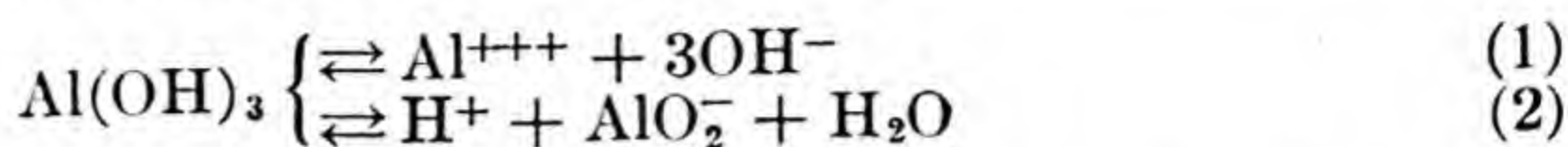
We have learned that the elements in Group I of the Periodic Table are metals that form strong bases. Likewise, the metals in Group II, the alkaline earth elements, are strong base formers. The elements in Group VII, the halogens, are acid formers. Non-metals, in general, form acids. We have studied also the acids of nitrogen, Group V, and of sulfur, Group VI. We know, then, that the elements on the extreme left-hand side of the Periodic Table are base formers, while those on the right-hand side are acid formers. We might ask whether the properties of the elements change abruptly from one class to the other, or whether there is a gradual change from the properties of a true metal to those of a nonmetal.

The elements in Group III are classified as metals but they have some nonmetallic properties. Boron, for example, forms halides, such as BF_3 , a colorless gas; BCl_3 , a colorless liquid; BBr_3 , a colorless viscous liquid; BI_3 , a white crystalline solid. In these compounds boron acts like a metal. We have already studied the acids of boron, in which the element plays the part of a nonmetal. Aluminum has stronger metallic properties than boron, but it also has a dual nature. Aluminum hydroxide is a weak base, and it is very slightly soluble in water. It can be neutralized by an acid according to the equation



If, however, a solution of sodium hydroxide is gradually added to a suspension of aluminum hydroxide, the precipitate disappears. Aluminum hydroxide reacts with the base, forming water and the ions of a salt, sodium aluminate, Na_3AlO_3 . In other words, in the presence of an acid, aluminum hydroxide acts like a base; in the presence of a strong base, aluminum hydroxide acts like an acid. A solution of ammonium hydroxide does not react with aluminum hydroxide as does sodium hydroxide. Ammonium hydroxide does not yield hydroxide ions in sufficient concentration to react with aluminum hydroxide. We may write the formula

for aluminum hydroxide as $\text{Al}(\text{OH})_3$ or as H_3AlO_3 . In the latter form its reaction with a base is more readily understood. Aluminum hydroxide ionizes in two ways as follows:



An acid removes hydroxide ions, thereby promoting reaction (1). A base removes hydrogen ions and promotes reaction (2).

Nature of amphoteric substances. Elements and compounds which have both basic and acidic properties are said to be *amphoteric*. Boron and aluminum are amphoteric elements because each acts like a metal in some of its compounds, and like a non-metal in others.

Aluminum hydroxide is a typical amphoteric substance, since it neutralizes both strong bases and strong acids, forming water and a salt in each case.

We shall find that many of the elements contained in the groups which are not at the extreme left or right of the Periodic Table are amphoteric in character.

Questions and Exercises

1. Explain the amphoteric character of some elements.
2. Scandium is next to aluminum in Group III of the Periodic Table. Write equations showing the amphoteric property of scandium hydroxide, $\text{Sc}(\text{OH})_3$.
3. Do you think rubidium hydroxide and radium hydroxide are amphoteric substances? Give reasons for your answers.

UNIT XIII

Subgroup I of the Periodic Table:

Copper, Silver, and Gold

PART 1

Copper

Copper, silver, and gold, together with the alkali metals, constitute the first group of the periodic system. The alkali metals comprise the main group, and copper, silver, and gold form a subgroup. Like the alkali metals (and like all other metals), copper, silver, and gold conduct an electric current and have metallic lusters. In almost all other respects they are unlike the members of the main group. The alkali metals are softer, less dense, and more reactive. Copper, silver, and gold are so unreactive that they are known as *noble* metals.

Group I	
Li	
Na	
K	Cu
Rb	Ag
Cs	Au
Main group	Sub-group

The table below shows some of the physical properties of these metals.

	Copper	Silver	Gold
Symbol.....	Cu	Ag	Au
Atomic number.....	29	47	79
Atomic weight.....	63.57	107.880	197.2
Isotopes.....	63, 65	107, 109	197
Electron structure:			
1st shell.....	2	2	2
2nd shell.....	8	8	8
3rd shell.....	18	18	18
4th shell.....	1	18	32
5th shell.....	—	1	18
6th shell.....	—	—	1
Density.....	8.92	10.5	19.3
Melting point, °C.....	1083	960.5	1063
Boiling point, °C.....	2310	1950	2600

Copper is found in the free state in nature. There are large deposits of native copper in Michigan on the shores of Lake Superior. These deposits were worked by the early American Indians. The largest mass, found in 1855, weighed 840,000 lb. It is now kept in the Smithsonian Institute.

Most copper, however, is found in the combined state, the principal compounds found in nature being the sulfide and the basic carbonate. The normal copper carbonate, CuCO_3 , is not known. The compounds containing copper and the carbonate radical also contain the hydroxyl radical. A copper ore called *malachite*, for example, has the formula $\text{Cu}_2(\text{OH})_2\text{CO}_3$ or $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. This ore is a *basic carbonate*. *A basic salt of any metal is a combination of a normal salt with a hydroxide or oxide of the metal.*

The United States produces about 25 per cent of the world's supply of copper. Chile ranks second, with 17 per cent, and Canada third, with 12 per cent.

The feathers of certain birds contain traces of copper. In the blood of oysters, lobsters, cuttlefish, and scorpions copper instead of iron is the essential metal atom.

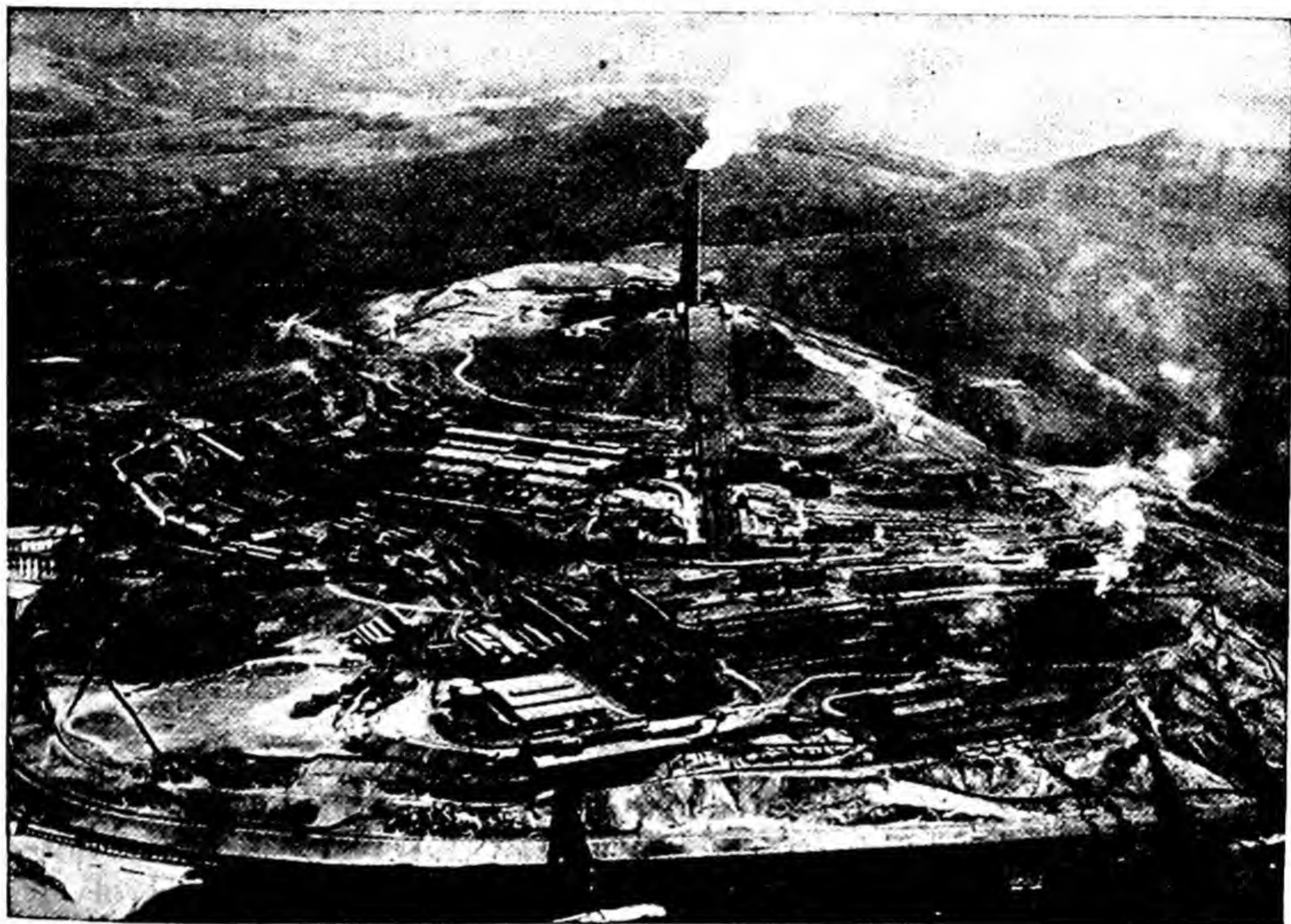
The extraction of copper from its ores. Copper ores from different localities have different compositions, and the method of extracting copper from one kind of ore usually cannot be applied to another ore without some modification. Most of the copper produced in the United States is extracted from sulfide ores, and these ores contain less than 10 per cent copper, with some iron sulfide and arsenic sulfide, but they are frequently accompanied by small quantities of gold, silver, antimony, bismuth, selenium, and tellurium. The Montana process of treatment is a typical one. It consists in (1) concentration of the ore, (2) roasting, (3) smelting, (4) reduction, and (5) refining.

Concentration of the ores is carried out by means of the flotation process. The ore is first crushed and ground to a fine powder. It is next mixed with oils, which adhere to the metal-bearing particles only. The mixture is run into tanks of water which are stirred rapidly, so that air is entrapped and forms a froth. This froth is easily separated from the earthy part of the ores. The water is removed by filtration, resulting in a concentrate which contains about 95 per cent of the copper and only about one-third of the nonmetallic part of the ore.

The ore is next *roasted*. By roasting the ore (heating it in the presence of air), the iron sulfide is converted into iron oxide and sulfur dioxide. The sulfur dioxide escapes as a gas. Some of the copper sulfide is changed to the oxide in the roasting process.

Smelting is accomplished by mixing the roasted ore with limestone and some of the unroasted ore, and heating the mixture in a blast furnace. In this process the iron oxide combines with silica and is removed as a slag, which floats on the surface of the molten mass of cuprous sulfide, called *matte*. The matte contains from 15 to 60 per cent copper, a small amount of iron sulfide, and usually some gold and silver in addition to cuprous sulfide.

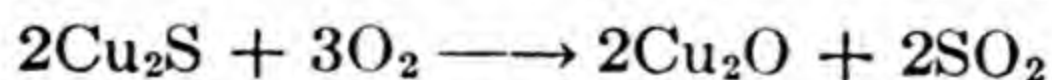
Reduction. The matte is then melted in a Bessemer converter, and air is blown through it to remove the sulfur in the form of



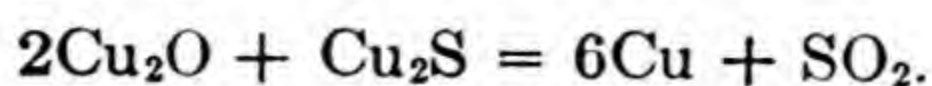
Courtesy, Anaconda Copper Mining Co.

Fig. 158. Copper smelting and refining.

sulfur dioxide. The iron oxide which is formed at the same time combines with the silica lining of the converter. At intervals the converter is tilted, and the slag is allowed to flow off. The material left is composed of about 78 per cent copper, having approximately the composition Cu_2S . As the blast continues, oxygen begins to react with the copper sulfide, changing it to copper oxide:



As soon as cuprous oxide forms, it reacts with cuprous sulfide, forming metallic copper:



To remove any unchanged copper oxide, the molten metal is stirred with poles of green wood. The gases generated by the heated wood reduce the last traces of copper oxide to copper. The metal, called "blister copper" because of the air bubbles it contains, is cast into huge sticks. The composition of blister copper is about 99.3 per cent copper, with small amounts of arsenic, antimony, silver, gold, and other metals.

Refining is done electrolytically. In this process the sticks of the crude or impure metal are used as positive electrodes and strips of pure copper are used for the negative electrodes. The electrodes are immersed in a solution of copper sulfate, which serves as an electrolyte. When a current of electricity is passed through a refining cell of this kind, the copper of the positive electrodes (anodes) goes into solution, and pure copper deposits

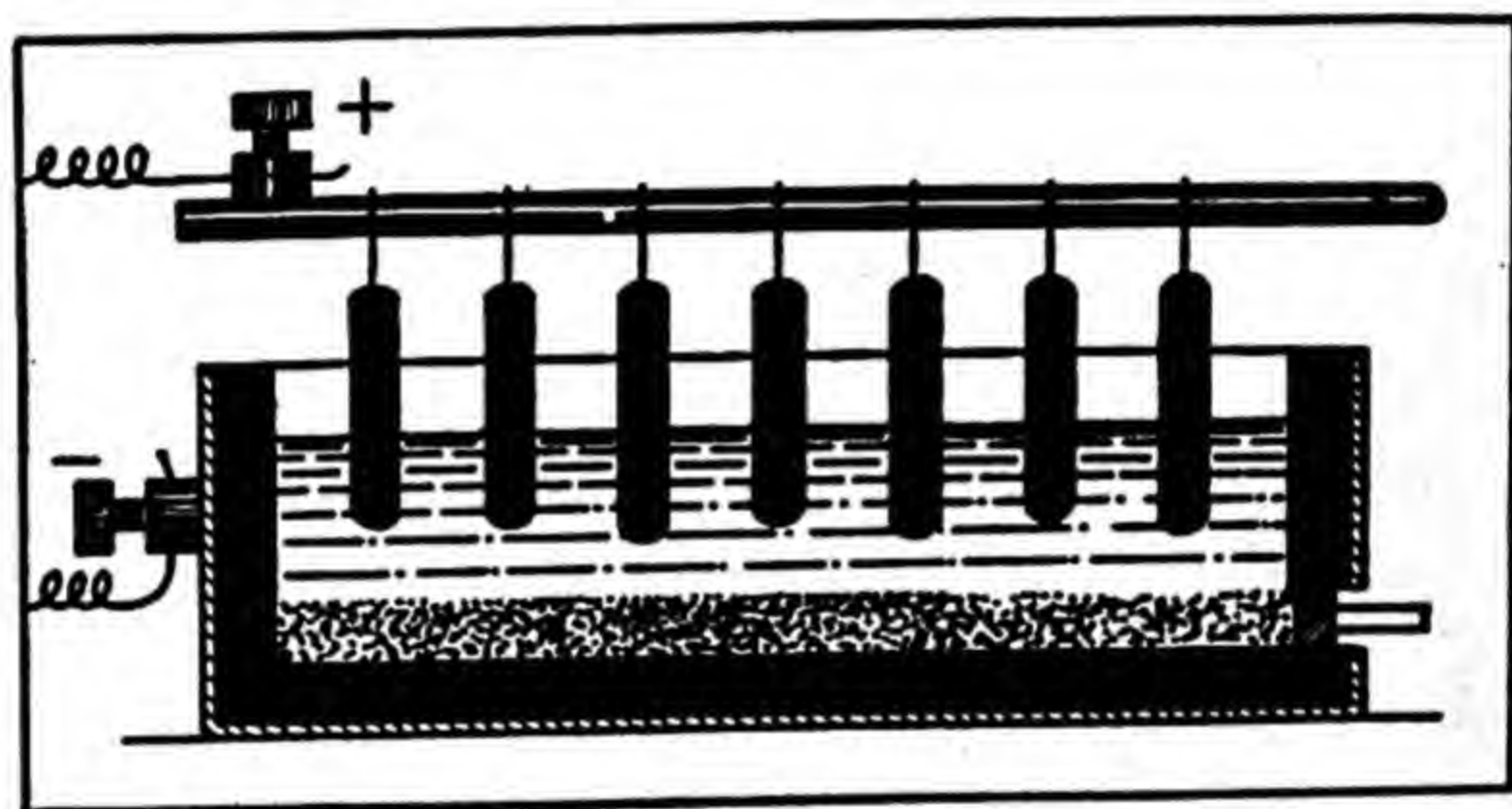


Fig. 159. Apparatus for the electrolytic refining of copper.

on the negative electrodes (cathodes). The impurities, including the gold and silver, settle to the bottom of the cell or tank. These are usually recovered in sufficient amount to pay for the electrolytic refining.

Physical properties. Copper is a reddish-brown metal which melts at 1083°C . and has a density of 8.92 g. per cubic centimeter. It is not very hard and it can be rolled into sheets, drawn into wire, and hammered into various shapes. It is a very good conductor of electricity, and this property makes it one of our most important metals. The conductivity of copper is decreased by certain impurities; consequently, for electric wiring very high purity is essential. Arsenic is one of the most troublesome impurities in this respect. If it is present to the extent of 0.03 per cent, it lowers the conductivity of the copper 14 per cent. Copper, silver, aluminum, and gold are excellent conductors. These metals are also good conductors of heat. The conduction of heat and electrical conductance always go together. A metal

that is a good conductor of electricity is also a good conductor of heat.

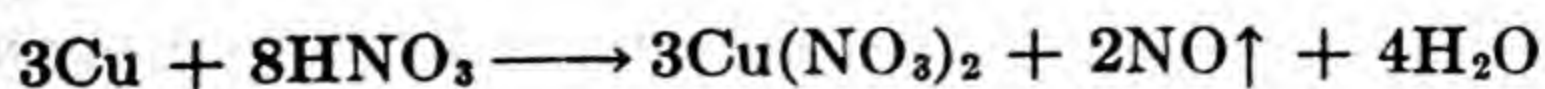
Uses. Most of the world's supply of copper is used in the electrical industries. Enormous quantities of this metal are employed each year for the construction of cables and new transmission lines for electricity. On account of its ability to conduct heat and to withstand corrosion, copper is used extensively in the manufacture of heating coils, boilers, large-sized cooking utensils, and commercial chemical apparatus. It is employed also to a large extent in the manufacture of alloys.

COPPER ALLOYS

<i>Name</i>	<i>Composition (per cent by weight)</i>
Brass.....	Copper, 60-75; zinc, 40-25
Bronze.....	Copper, 75-90; tin, 15-10; zinc, 10-5
German silver.....	Copper, 50-60; zinc, 25; nickel, 25-15
Gun metal.....	Copper, 90; tin, 10
Aluminum bronze.....	Copper, 90-98; aluminum, 10-2
Aluminum bronze.....	Copper, 30-98; aluminum, 0.6-25; iron, 0-10; zinc, 0-37; nickel, 0-20
Bell metal.....	Copper, 75-80; tin, 25-20
Nickel coin.....	Copper, 75; nickel, 25

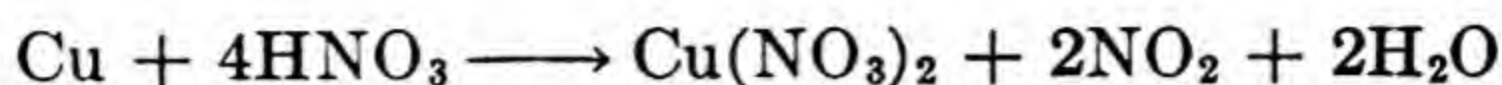
Books are often printed from plates made by the electrotyping process. In this process the ordinary type is set as usual. A wax impression of each page of the type is made, and the wax mold or impression is then coated with graphite to make it a conductor of electricity. A thin layer of copper is then deposited electrolytically over the graphite. A perfect copy of the type is made in this way. The back of each copper plate is hollow, and this is filled with lead to give added strength to the plate.

Chemical properties. At ordinary temperatures copper is unchanged by air or water. When exposed to moist air, copper corrodes, forming a mixture of green, basic salts. The colored substance may contain the basic chloride, sulfate, or carbonate depending upon conditions under which it is formed. Copper does not react with hydrochloric acid or with dilute sulfuric acid unless some oxidizing agent is present also. In other words, it does not replace hydrogen ions. Hydrogen ions cannot take electrons away from copper atoms. The metal, therefore, fails to dissolve in dilute hydrochloric acid. Copper reacts with nitric acid and with concentrated sulfuric acid, for these are oxidizing agents as well as acids. In these reactions hydrogen gas is not evolved. With dilute nitric acid the reaction proceeds as follows:

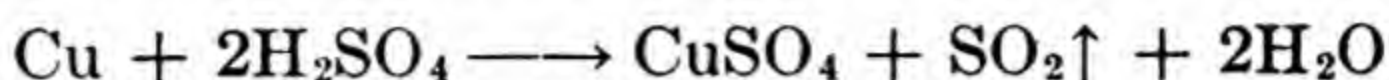


When copper reacts with *concentrated* nitric acid, nitrogen dioxide

is given off:

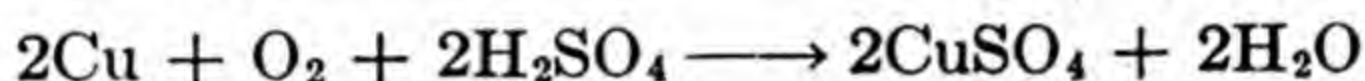


With *concentrated* sulfuric acid, copper reacts as follows:



Compounds. Copper forms two classes of compounds. In the cuprous compounds the copper has a valence of 1, and in the *cupric* compounds its valence is 2. The cupric compounds are the more stable and the more important ones.

Copper sulfate, *blue vitriol* or *bluestone*, has the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Five molecules of water are associated with each molecule of copper sulfate in the crystalline compound. When the blue crystals of this compound are heated, the water is driven out and white anhydrous copper sulfate, CuSO_4 , is formed. Copper sulfate may be made from copper and *dilute* sulfuric acid under conditions that permit oxidation by the air. Copper scraps are converted into copper sulfate by alternately dipping the scraps into dilute acid and exposing to air. The complete reaction is indicated by the equation



In this reaction no sulfur dioxide is formed, as would be the case if concentrated acid were used, and less acid is required.

A mixture of lime and copper sulfate, known as *Bordeaux mixture*, is used for spraying plants to prevent the growth of fungi. Copper sulfate is used also in the purification of water. Large reservoirs of water often become infected with small plants known as algae which discolor the water and give rise to bad odors. Very small amounts of copper sulfate added to these ponds or reservoirs kill the algae. The concentration of copper sulfate needed for this purpose is too small to impart a taste to the water.

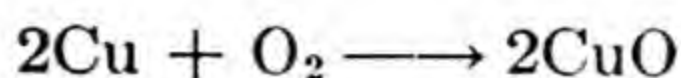
The annual production of copper sulfate in the United States is about 46,000,000 lb., which accounts for the use of nearly 12,000,000 lb. of the metal. Copper sulfate is by far the most important commercial salt of copper.

Cupric nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and cupric chloride, CuCl_2 , are both soluble copper salts. The solid nitrate is blue and the solid chloride green, but dilute solutions of all cupric salts are blue. The Cu^{++} ions are responsible for the blue color of the solutions.

Cupric oxide, CuO , is a black compound which is insoluble in water. It is easily reduced by heating it with hydrogen:

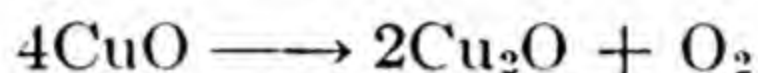


Cupric oxide is made by the action of oxygen of the air upon heated copper:



It is used for the production of green and blue colors in glass, porcelain, and stoneware.

Cuprous oxide, Cu_2O , is a red-colored compound which can be made by heating cupric oxide in the absence of oxygen:



Cuprous oxide is used in the manufacture of red glass, the red glaze on porcelain, and some photoelectric cells.

Tests for copper. Ammonia reacts with copper salts in solution, producing a complex compound of ammonia molecules and copper ions, $\text{Cu}(\text{NH}_3)_4^{++}$. The complex ions impart to the solution a very deep blue color. Cuprous ions are colorless, but such solutions give a blue color when exposed to the air. Cupric solutions are green when concentrated, but give the characteristic blue on dilution. Hydrogen sulfide precipitates black CuS . This precipitate dissolves in concentrated nitric acid, liberating sulfur and oxides of nitrogen.

Questions and Exercises

1. Write the equations for the refining of a sulfide ore of copper.
2. What is blister copper? Matte?
3. Why is copper refined electrolytically?
4. Write the equation for the reaction of copper with (a) concentrated nitric acid; (b) dilute nitric acid; (c) concentrated sulfuric acid.
5. Name two uses for blue vitriol.
6. Calculate the percentage of water of hydration in blue vitriol.
7. Name six alloys of which copper is a constituent.
8. Explain the flotation process used in the production of copper.
9. Describe two methods for dissolving copper. What products are formed in the two processes?
10. Explain the process of copper plating.
11. Account for the fact that all cupric salts form blue solutions. In the crystalline form some cupric salts are not blue.
12. What is meant by native copper? Is copper found in this form in the United States?
13. How can you prepare copper sulfate from cupric oxide?

PART 2

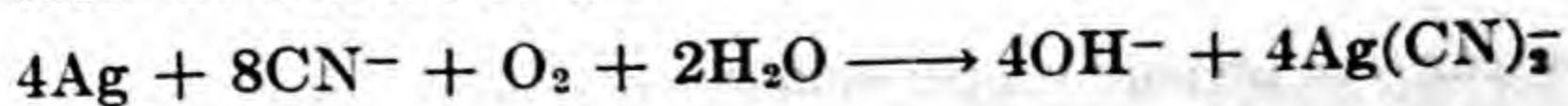
Silver

Occurrence. For thousands of years silver has been used for jewelry and for ornamental purposes. It is the commonest and the cheapest of the precious metals. It is found to a large extent as free silver. It occurs also as the sulfide, Ag_2S , but this is usually mixed with the sulfides of other metals, particularly copper. It is found to a small extent in the form of the chloride, AgCl . Most of the world's silver is mined on the North American continent, Mexico being the leading silver-producing country.

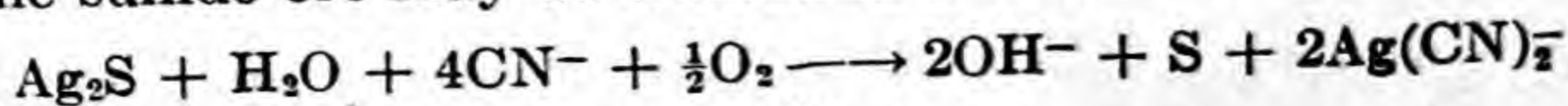
Extraction from its ores. A considerable quantity of silver is recovered as a by-product in the electrolytic refining of copper. As the impure copper anodes dissolve in the electrolytic cell, the gold, silver, and other impurities drop to the bottom of the cell as mud. The gold and silver are extracted from the mud by one of the methods employed for the treatment of silver ores.

Lead ores often contain considerable quantities of silver, and this silver dissolves in the lead when the lead is extracted from the ore. To recover the silver from the lead, a small amount of zinc is added to the molten mass. Zinc does not dissolve in molten lead but floats as a liquid layer on the surface of the lead. Silver is 3000 times as soluble in zinc as in lead; so if the melted mixture of lead and zinc is stirred, most of the silver leaves the lead and dissolves in the zinc. The zinc which contains the silver separates as a liquid layer above the molten lead. The zinc and silver solidify as the mixture is cooled, and the solid layer is skimmed off. The zinc and silver are separated by distilling the zinc. This method of recovering silver from lead is known as *Parke's process*.

A method that is very generally used for recovering free silver and gold from ores is that of leaching the crushed ore with a solution of sodium cyanide. In the presence of air a cyanide solution dissolves both silver and gold to form soluble complex cyanide salts of these metals.



The sulfide ore may be treated in a similar manner:



The silver is precipitated from the solution by the addition of zinc. The zinc replaces the silver in solution, and the silver precipitates in the free state.

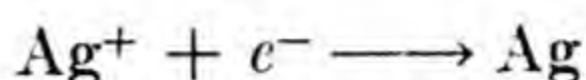
Properties. Pure silver is soft and can be hammered or rolled into any desired shape. It is the most lustrous of the metals; in other words, its ability to reflect light is greater than that of other metals. In pure dry air it does not tarnish, although indoors and in contact with the human skin it does so slowly because of reactions with sulfur compounds. In the manufacture of jewelry, silver has been replaced to a large extent by the more expensive metals, platinum and white gold (an alloy of gold and nickel). Silver is somewhat heavier than copper, and it is the best known conductor of heat and of electricity. Its ability to conduct heat can be demonstrated by dipping both a solid silver spoon and a plated one in the same cup or vessel containing a hot liquid. The handle of the solid silver spoon becomes warmer than the other.

Uses. Silver is used principally in the manufacture of jewelry, cutlery, and coins, and in the electroplating industry. Silver is a very soft metal, and for that reason it is rarely used alone. To give the required hardness for coins and jewelry, silver is alloyed with copper. The United States silver coins contain 90 per cent silver and 10 per cent copper. Those of Great Britain contain 92.5 per cent silver and 7.5 per cent copper. This latter alloy is known as *sterling silver*. The so-called "sterling silver" used in jewelry, however, often contains as much as 20 per cent copper.

Mirrors are made by precipitating silver from an ammonia solution of a silver salt by some reducing agent, such as glucose. The silver solution and the one containing the reducing agent are mixed and poured over the glass surface to be silvered. The glass is then allowed to stand for some time in a warm place, and silver is gradually deposited on the surface of the glass as a bright reflecting film. The film of silver is dried and then lacquered to protect it from corrosion and damage. Silver is converted into silver bromide and silver chloride for use in the preparation of photographic films, plates, and papers.

Silver plating. Silver may be deposited electrolytically on many other metals. The method employed is similar to that used in the electrolytic refining of copper. The solution used in silver plating is made by dissolving silver nitrate in a solution of potassium cyanide. A solution of the complex salt $\text{KCN} \cdot \text{AgCN}$, or $\text{KAg}(\text{CN})_2$, is formed. The object to be plated and a strip of pure silver are dipped into this solution, and the two are connected to a battery. The object to be plated is charged negatively and the silver sheet positively (Fig. 160). Silver ions are attracted

to the surface of the negatively charged object, and here each positive silver ion acquires an electron and becomes an ordinary silver atom. A constant supply of electrons is delivered to the object by the battery. The reaction taking place on the surface of the object being plated is represented by the equation:



The battery draws electrons out of the pure silver electrode and

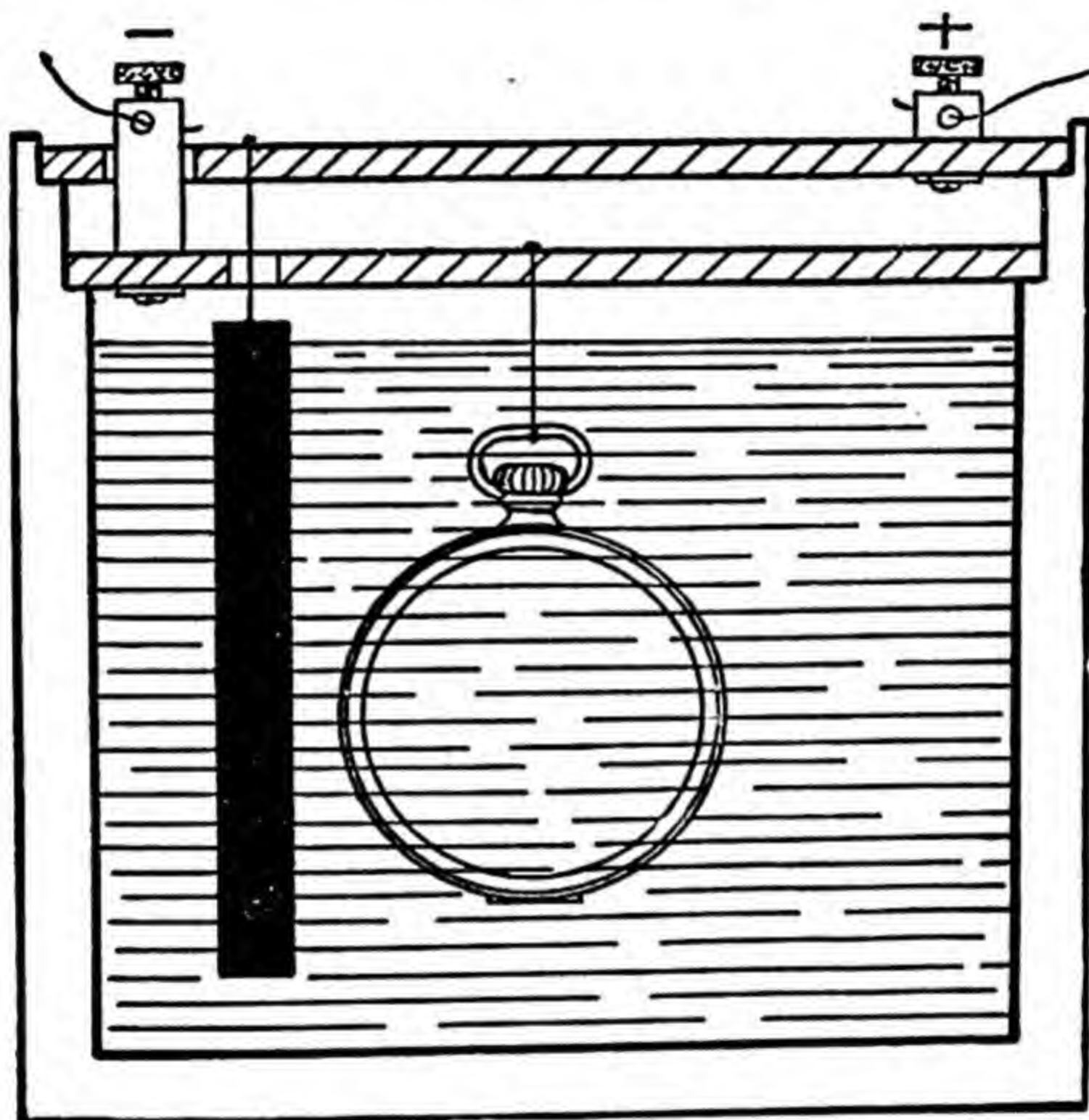


Fig. 160. Apparatus for silver plating.

thus promotes the formation of silver ions, which go into solution. The reaction at the positive electrode is:

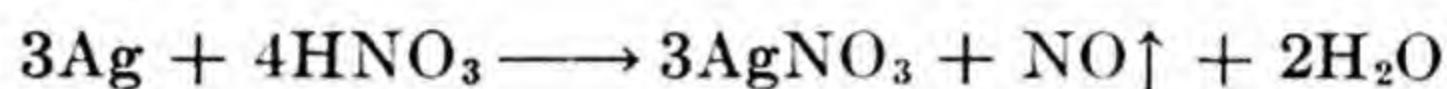


This is the exact reverse of the reaction taking place at the negative electrode. The net result is that silver enters the solution from the positive electrode and leaves the solution ("plates out") at the same rate on the negative electrode. The electric current transfers silver through the solution from the pure sheet of silver to the surface of the object to be plated, and transfers electrons through the wires and battery from the pure silver to the object to be plated.

Chemical properties. Silver does not dissolve in hydrochloric acid or in dilute sulfuric acid. In nitric acid and in concentrated

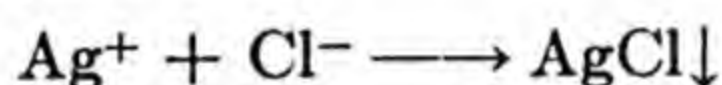
sulfuric it dissolves readily. (Compare this behavior with that of copper. See page 379.) Hydrogen sulfide reacts upon silver in the presence of moist air to produce a black insoluble silver sulfide, Ag_2S . The formation of this compound accounts for the tarnishing of silverware in homes. City gas usually contains traces of hydrogen sulfide, and some of this remains unchanged in the burning of the gas. Sulfur compounds in eggs and in some other foods also cause silverware to tarnish.

Compounds. Silver nitrate is the most useful soluble salt of silver. Other salts of silver may be prepared from it, usually by direct precipitation. Silver nitrate is made by the action of nitric acid upon silver:

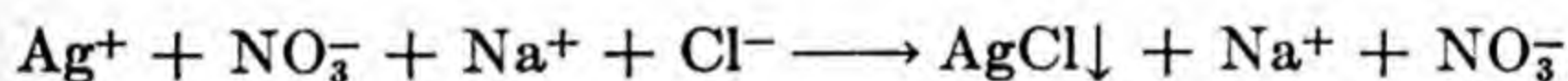


Silver nitrate is very soluble in water, and it is easily reduced to free silver by contact with organic compounds. For example, a solution of silver nitrate reacts with the skin, producing a black stain of free silver.

The silver halides are all insoluble in water. Silver chloride is made by the addition of a solution containing chloride ions to one containing silver ions:



Or:



Test for silver. This reaction serves as a test for chloride ions or for silver ions. In a test for chloride ions, nitric acid and silver nitrate are added to the sample to be analyzed. In a test for the presence of silver ions, hydrochloric acid is added to the solution. The test is positive if a white precipitate forms and turns dark when exposed to sunlight. Silver chloride is soluble in ammonia and in a solution of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$. The soluble compounds formed are the complex ions $\text{Ag}(\text{NH}_3)_2^+$ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{--}$, respectively. Sodium thiosulfate is commonly called "hypo." It is used by photographers for fixing negatives; that is, for dissolving from the negatives the unchanged residues of silver bromide.

Silver bromide, a light-yellow, insoluble salt, is used extensively in the preparation of photographic plates and films. It dissolves in ammonia with difficulty, but it dissolves readily in a solution of sodium thiosulfate.

Photography. Silver bromide is reduced to free silver by the organic compounds used as photographic developers. The reaction takes place more rapidly with silver bromide that has been

exposed to light than with silver bromide that has been kept in the dark. This principle is employed in photography.

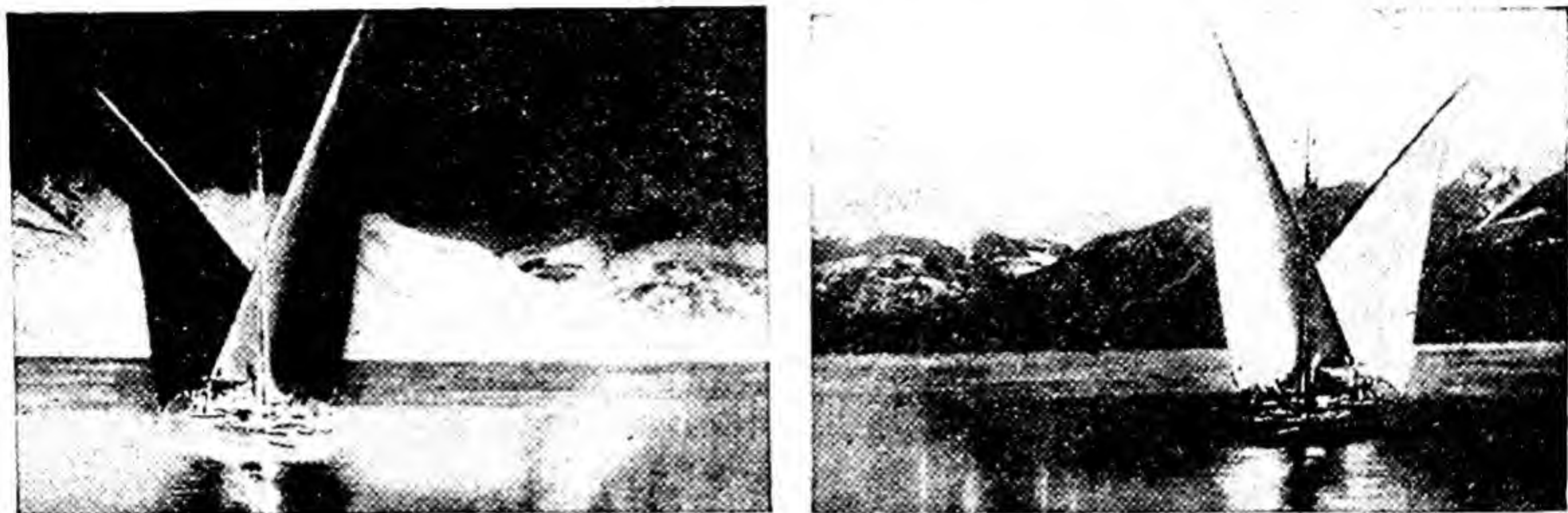


Fig. 161. Two stages in the process of making a photograph. Left, the negative; right, the positive.

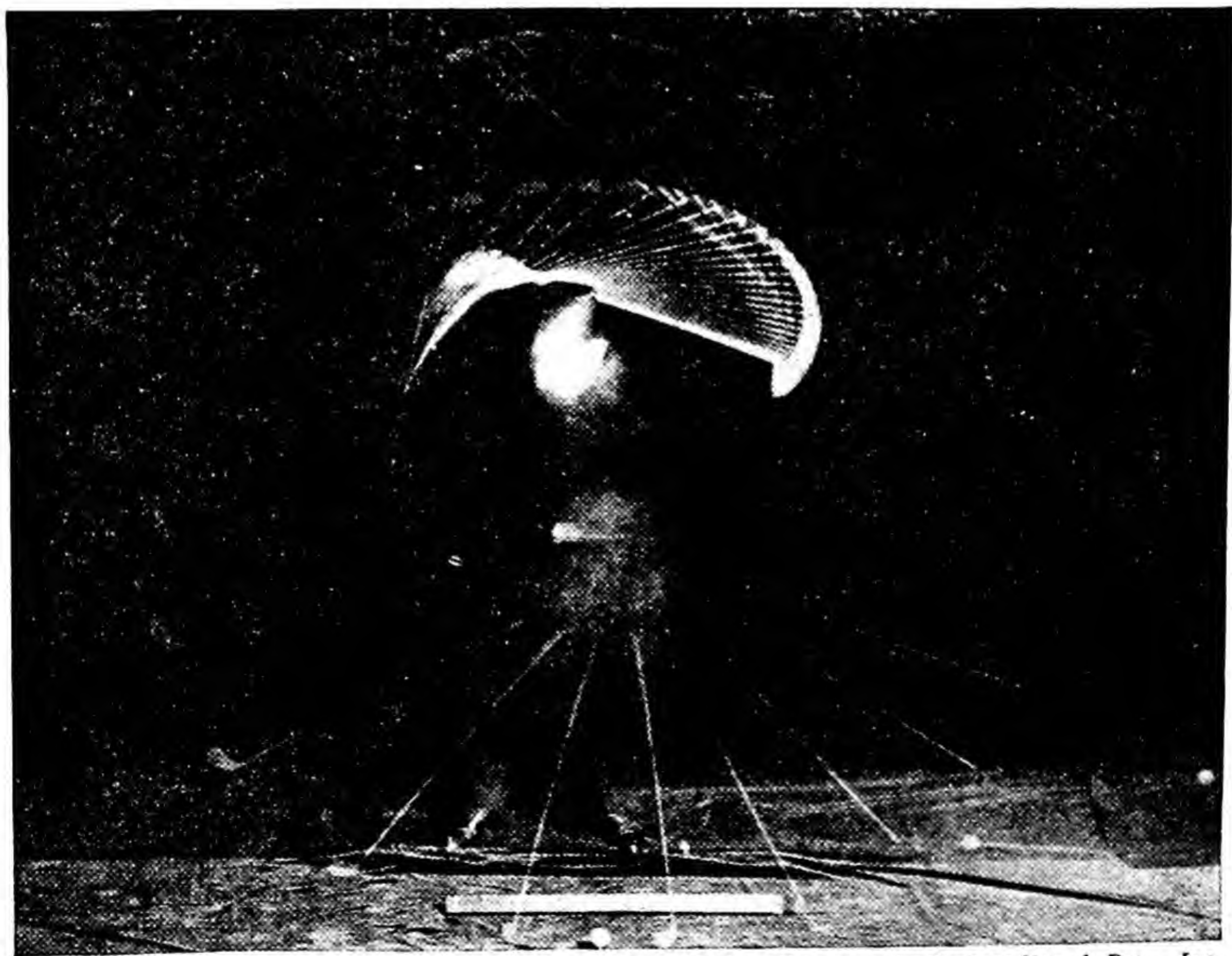


Photo by Harold E. Edgerton, Mass. Inst. Tech. *Courtesy, A. E. Spalding & Bros., Inc.*

Fig. 162. Many pictures of Bobby Jones taken one after another on the same plate. Duration of each exposure $1/100,000$ of a second. Time between exposures $1/100$ of a second.

In the making of a photographic plate, silver bromide is precipitated in the dark by mixing a solution of silver nitrate with a solution containing a soluble bromide. The resulting precipitate

is incorporated in a warm gelatin solution, and this is allowed to flow over a glass plate or a celluloid film. On cooling, the gelatin hardens, holding the grains of silver bromide imbedded in it. The plate, or film, is then ready for exposure to light.

When a photographic plate is exposed by the opening of the lens of the camera, those grains which are struck by light become sensitized in such a way as to make them easily reduced by a developer. An electrical instrument called a *stroboscope* produces flashes of light of short duration and at any desired intervals. With the aid of this instrument much shorter exposures can be made than with an ordinary shutter. The intervals between the flashes can be controlled also. When the light is to be supplied by a stroboscope the camera lens is left wide open, the time of exposure being determined entirely by the duration of the flash. See Figures 20 and 162.

Developing. The exposed plate is immersed in a solution of a developer, and the image photographed appears on the plate within a few seconds or a few minutes. The light portions of the object photographed appear black on the negative, for fine particles of silver are black. The dark portions of the object photographed are light on the photographic plate. The developing process must be carried out in the dark or in a red light. Red light does not affect the silver bromide.

Fixing. To render the developed image permanent, all unreduced silver bromide must be removed from the plate, or the whole plate will subsequently become black. This is accomplished by immersing the plate in a solution of sodium thiosulfate, or *hypo*, $\text{Na}_2\text{S}_2\text{O}_3$, which dissolves the unchanged silver bromide and does not dissolve the free silver that has been formed through the action of the developer. When this process is completed, the plate, known as the *negative*, may be exposed to light and, after washing and drying, it is ready to be used in the printing process.

Printing. The photograph is made on paper which, like the plate, is covered with a gelatin film containing silver bromide or silver chloride, or a mixture of the two. The print is made by placing the negative next to the paper and exposing the paper to light through the negative. The dark portions on the negative act as screens and prevent light from striking the paper in these parts. The paper is then immersed in a solution of a developer. The dark regions of the negative produce light areas on the paper, and a positive image of the object photographed is produced.

Ordinary photographic plates and films are sensitive to blue, violet, and ultraviolet light. White light contains all of these. Plates may be made sensitive to green and yellow light by the

addition of a colored dye to the gelatin. Such plates are known as *orthochromatic* plates. Plates or films may be made sensitive to red light also by the addition of suitable dyestuffs.

Questions and Exercises

1. Name two silver salts that are used in the manufacture of photographic supplies.

2. When an object is photographed, the light portions of the object appear dark in the negative. Explain this phenomenon.

3. Silver salts are easily *reduced* to free silver. The reducing agent is, at the same time, *oxidized* to some new substance. What are the oxidizing agents and the reducing agents used in the following reactions: (a) formation of a mirror, (b) production of a silver stain on the hand, (c) precipitation of silver in producing a photographic negative?

4. Explain the use of zinc in the extraction of silver from lead.

5. Mustard tarnishes silver. Name one element that is present in mustard.

6. What weight of silver chloride would be precipitated if an excess of silver nitrate were added to a solution containing 10 g. of common salt?

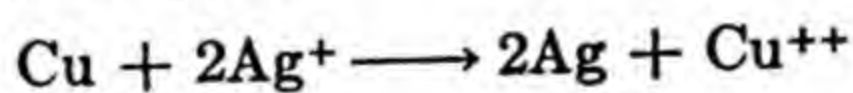
7. When hydrogen sulfide gas is passed into a solution of silver nitrate, a black precipitate is formed. Write an equation for the reaction.

8. Write the equation for the reaction of each of the following on metallic silver: (a) dilute nitric acid; (b) concentrated nitric acid; (c) concentrated sulfuric acid; (d) dilute hydrochloric acid.

9. Explain in words (not in equations) the chemistry of photography.

10. Describe the process of silver plating.

11. A United States silver coin weighing 6.11 g. (a quarter) was dissolved in nitric acid. What compounds were formed? The silver in the solution was precipitated by adding pure copper:



What weight of copper was needed to precipitate all the silver?

PART 3

Gold

Occurrence. It is believed that gold was the first metal to be isolated and used by primitive man. It is found free in nature; it is attractive in color; and it is one of the most durable of our metals. Because of these properties and its scarcity, it was in ancient times regarded as the most precious metal, and it still enjoys the same esteem.

Gold is frequently found associated with the sulfide ores of copper, silver, lead, and zinc. Sylvanite, a compound of gold, silver, and tellurium, is found in deposits in Transylvania and Colorado.

The world's annual output of gold is approximately 35,000,000 fine ounces. The United States produces about 12 per cent of this amount. It has been estimated that 40,000 tons of gold have been taken from the earth since the discovery of America.

Recovery. Gold is usually found in tiny flakes, which may be scattered through veins in quartz. From time to time a very rich vein is discovered, as for example in the Comstock Lode at Virginia City, Nevada, where, it is claimed, one pocket yielded in five days gold valued at \$11,000,000.

As quartz rocks disintegrate, the fine flakes of gold are scattered along the beds of rivers. Placer mining is going on now in many old river beds that are miles from the present sites of the streams. The sands in the river beds of the Sierra Nevada Mountains of California contain deposits of fine gold. Much of this is being recovered by "panning" or by passing the sand through sluice boxes in a stream of water. These boxes have corrugated bottoms and, as the ore passes through, the heavier gold settles to the bottom and lodges in the sluices or corrugations of the box. The concentrated ore is then passed over mercury to permit the gold to amalgamate with the mercury. The mercury is removed from the gold by distillation.

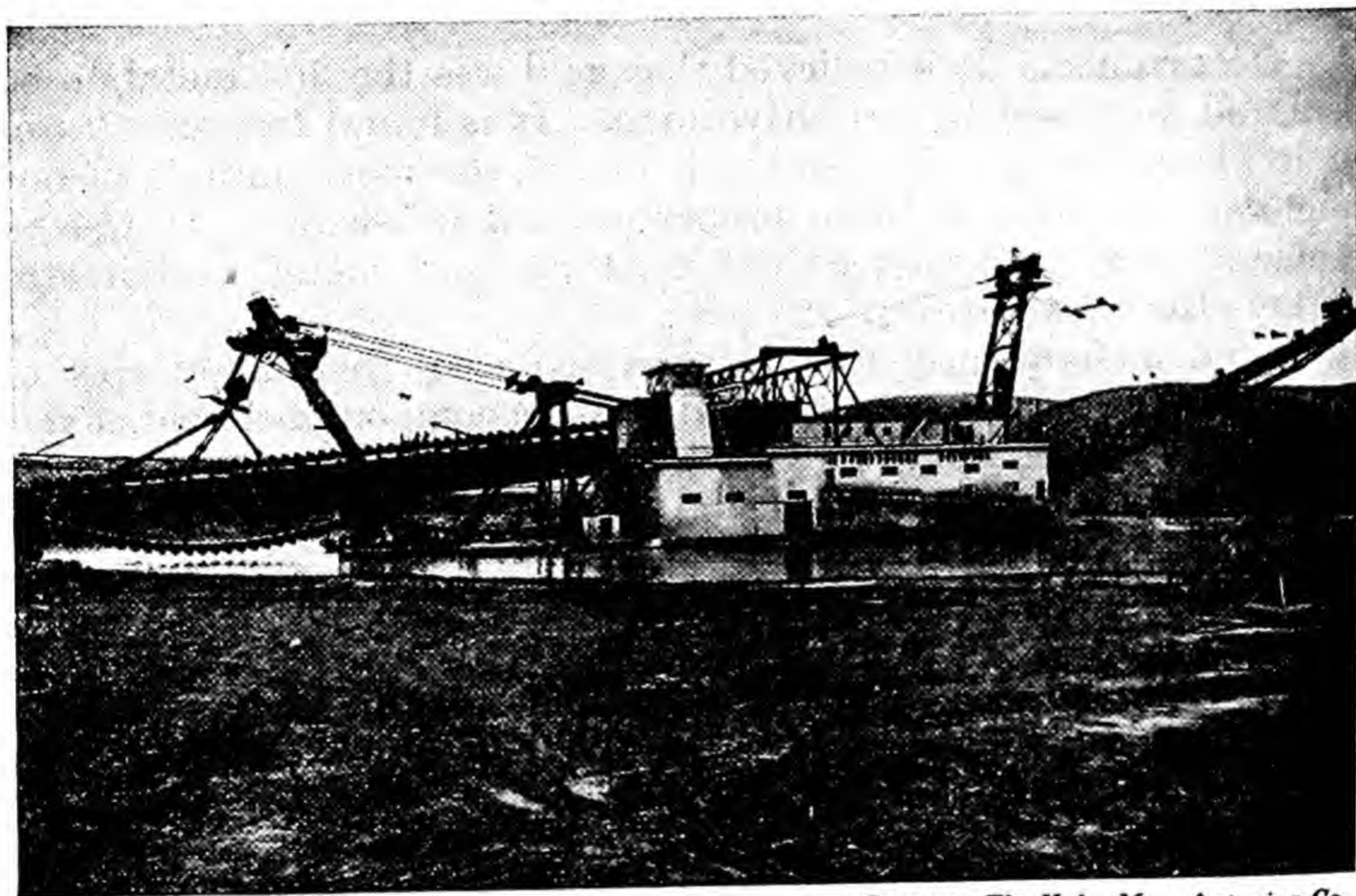
Metallurgy. There are three modern methods for obtaining gold from its ores.

The chlorination process. This depends upon the ability of chlorine to combine with gold, forming the soluble gold chloride AuCl_3 . The chlorine is supplied in the form of liquid chlorine, or

bleaching powder and sulfuric acid. This method is said to obtain 95 per cent of the gold from the ore, but is seldom used now.

The amalgamation process. The ore is pulverized in the presence of water by a stamp mill. Mercury is then added, and a gold-mercury amalgam is formed. Finally, the mercury is distilled from the gold in iron retorts.

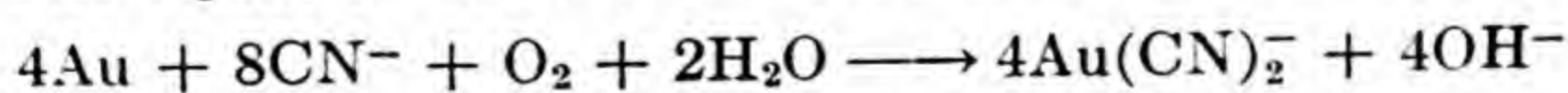
The cyanide process. This method of isolating gold is similar to that used for obtaining silver. (See page 382.) It has proved



Courtesy, The Yuba Manufacturing Co.

Fig. 163. Machinery for obtaining gold from the bed of a river. This dredge weighs 3750 tons. It digs to a depth of 124 feet below water level.

successful even when applied to low-grade ores. It has greatly increased the world's production of gold since its introduction in 1889. The equation for the reaction is as follows:



The complex cyanide is decomposed by zinc as in the case of silver cyanide.

Physical properties. Gold is yellow by reflected light, and green by transmitted light. It is soft and can be rolled, hammered, and worked into intricate designs. It is so malleable and ductile that sheets of gold less than one-millionth of an inch thick can be made, and 1 lb. of gold is sufficient to make 500 miles of wire. Such a wire resembles the strands of a spider web. In the pure state gold is too soft to be used for coins or jewelry; it is alloyed

with some other metal to harden it. The composition of gold in jewelry, or its fineness, is expressed in terms of carats, pure gold being 24 carats. So-called 18-carat gold is composed of 18 parts of gold and 6 parts of copper or silver, and 14-carat gold contains 14 parts of gold and 10 parts of copper or silver by weight. Gold coins contain 90 per cent gold and 10 per cent copper. Gold is one of the heaviest of the metals. It has a density of 19.3 g. per cubic centimeter; that is, it is 19.3 times as heavy as water or almost twice as heavy as silver. Gold is a very good conductor of electricity.

Chemical properties. Gold is so inert that it is not attacked by pure hydrochloric acid, nitric acid, or sulfuric acid. It will, however, dissolve in a mixture of concentrated nitric acid and hydrochloric acid, forming the compound HAuCl_4 or $\text{AuCl}_3 \cdot \text{HCl}$. The mixture of concentrated hydrochloric and nitric acids is known as *aqua regia* (royal water).

Uses. Besides being used in the manufacture of jewelry and coins, the metal is used extensively for gold plating. The process is like that described for silver plating, the solution used being a complex cyanide of gold and potassium.

Gold forms several alloys in common use. Copper alloys are yellow or red. White gold contains palladium, nickel, or zinc alloyed with gold. Green gold contains silver or cadmium. Blue gold is an alloy of gold with iron. Purple gold contains aluminum and gold.

Questions and Exercises

1. Why does gold exist in the free state in nature, while a metal like sodium does not?
2. Are the elements of the first main group of the periodic system found in the free state?
3. The elements of the first subgroup are *malleable* and *ductile*. Define each of the words printed in italics.
4. Specify two uses for each of the elements of the first subgroup in the periodic system.
5. Is there a solvent for gold?
6. Describe the action of each of the acids HCl , HNO_3 , and H_2SO_4 on each of the elements in the first subgroup of the periodic system.
7. High-frequency currents, such as those used in radio transmission, travel through the surface layers of a conductor and not through its interior. Explain why the wires used in some radio aerials are coated with a thin layer of gold or silver.
8. Name the three modern methods for obtaining gold from its ores. Describe each briefly.

PART 4

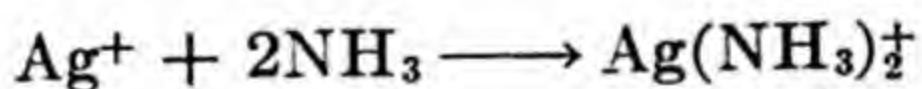
Complex Ions of Copper and Silver with Ammonia

The copper-ammonia ion. When ammonium hydroxide is added slowly to the solution of a copper salt, a green precipitate of basic copper sulfate is formed. The formula for this salt is $\text{Cu}_2(\text{OH})_2\text{SO}_4$. On the further addition of ammonia, the precipitate disappears and the solution becomes a beautiful azure-blue. The color is due to the copper-ammonia ion.



Many compounds of copper dissolve in ammonia, yielding the same ion. Copper sulfide is one of the few copper compounds that do not dissolve in ammonia.

The complex silver ion. Silver ion forms a compound with ammonia similar to that of the copper ion, but only two molecules of ammonia, instead of four, are attached to each silver ion:



The solubility of silver chloride and silver bromide in ammonia depends upon the formation of this ion. Silver iodide and silver sulfide do not dissolve in ammonia.

We usually think of silver chloride as being an insoluble substance, but actually no substance is entirely insoluble in water. If a liter of water is shaken for some time with silver chloride, we will find, on analysis of the solution, that there are both silver and chloride ions present. Most of the molecules remain in the solid state, but there is actually 0.00001 mole of silver ions in a liter of the saturated solution at room temperature. Silver bromide is less soluble than silver chloride, there being about 0.0000009 mole in a liter of solution. Silver iodide is still less soluble, with 0.00000001 mole per liter of solution. Silver sulfide is the least soluble of the four salts; that is, it contains the smallest number of silver ions in a liter of the saturated solution.

Why does ammonia dissolve silver chloride and silver bromide but not the other two salts mentioned?

When ammonia combines with silver ion, it leaves fewer free silver ions in the solution than would be present in a solution of either of the halides. If, for example, we add pure water to a precipitate of silver chloride in a beaker, some of the precipitate dissolves to saturate the solution. On the addition of ammonia, many of the dissolved silver ions are removed. More silver chloride then dissolves, trying once more to saturate the solution with silver chloride. Ammonia removes most of these, and so on, until the precipitate of silver chloride entirely disappears.

Silver bromide acts in a similar manner with ammonia, but dissolves more slowly. Silver iodide and silver sulfide are in equilibrium with fewer silver ions in their saturated solutions than the silver-ammonia complex ion leaves in the solution; hence ammonia cannot dissolve either of these highly insoluble salts. Silver bromide is a pale yellow solid. Silver iodide has a deeper yellow color. All silver halides turn black when exposed to light, because of the liberation of silver in a finely divided state.

UNIT XIV

Subgroup II of the Periodic Table: Zinc, Cadmium, and Mercury

PART 1

Zinc

Group II	
Be	
Mg	
Ca	Zn
Sr	Cd
Ba	Hg
Main group	Sub-group

The metals zinc, cadmium, and mercury comprise Subgroup II in the Periodic Table. Each of these elements has two valence electrons, and hence, in their compounds, a valence of 2. They differ in many respects from the elements in the main group. Their hydroxides are less basic, and the melting points are much lower than are those of the metals in the main group. The principle physical properties of these metals are listed below.

PHYSICAL CONSTANTS OF ZINC, CADMIUM, AND MERCURY

	Zn	Cd	Hg
Atomic number.....	30	48	80
Atomic weight.....	65.38	112.41	200.61
Isotopes.....	64, 66, 67, 68, 70	106, 108, 110, 111, 112, 113, 114, 116	198, 199, 200, 201, 202, 204
Electron structure:			
1st shell.....	2	2	2
2nd shell.....	8	8	8
3rd shell.....	18	18	18
4th shell.....	2	18	32
5th shell.....	—	2	18
6th shell.....	—	—	2
Melting point, °C.....	419.4	320.9	−38.87
Boiling point, °C.....	907	767	356.9
Density.....	7.14	8.6	14.19 at −40°

Occurrence. Zinc is too reactive to occur in the free state in nature. The mineral zinc blende, ZnS , is found associated with lead ores in Missouri, Oklahoma, Kansas, Montana, Idaho, Colorado, and Wisconsin. New Jersey also is a large producer of zinc; here the ores are composed of mixtures of the oxides of zinc, iron, and manganese. Some zinc silicate, zinc oxide, and zinc carbonate also are found in this district.

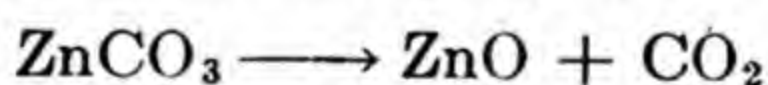
The world's annual production of zinc is nearly two million tons. The United States produces about one-third of the total. Other producers in the order of their yields are Belgium, Canada, Germany, and Poland.

Extraction from its ores. Zinc oxide ore is reduced by heating it with carbon. Coal is generally used as the source of carbon.



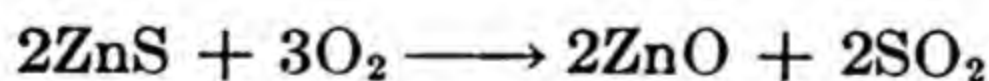
When zinc oxide and carbon are heated together in the absence of air, the zinc vaporizes, passes out of the hot chamber, and is obtained by condensation in a suitable cold chamber. Usually, however, a blast of air is admitted to the furnace, so that the zinc again burns to the oxide and is caught in huge canvas bags. The zinc oxide, freed in this way from less volatile oxides, is pure enough to be used in the paint and rubber industries and in the making of other zinc compounds.

Where the ore is other than the oxide, the first step in the metallurgy of zinc is the conversion of the ore to the oxide. The carbonate is converted to the oxide by heat alone:



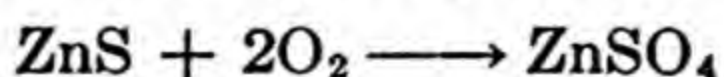
The oxide is then reduced to zinc with carbon as indicated above.

The sulfide ore is heated to a high temperature in the presence of air (roasted) and is thus converted into zinc oxide and sulfur dioxide:



The oxide is then mixed with carbon and heated. Zinc and carbon monoxide are the main products. The carbon monoxide is allowed to burn at the mouth of the receiver, and molten zinc collects within the receiver.

There is an expensive method in operation in Montana which produces very pure zinc. Zinc sulfide is roasted at a comparatively low temperature (under $600^\circ\text{C}.$) to produce zinc sulfate:



Some zinc oxide is also produced, but it is changed to zinc sulfate when the whole mass is leached with dilute sulfuric acid. Finally

the zinc is recovered from the zinc sulfate solution by electrolysis. Pure zinc is deposited on the cathodes, and oxygen is liberated at the anodes. Rods or plates of graphite are used for anodes, and the cathodes are made of aluminum or zinc. From time to time the process is stopped and zinc is scraped off the electrode, melted, and cast into ingots. Electrically produced zinc is 99.9 per cent pure.

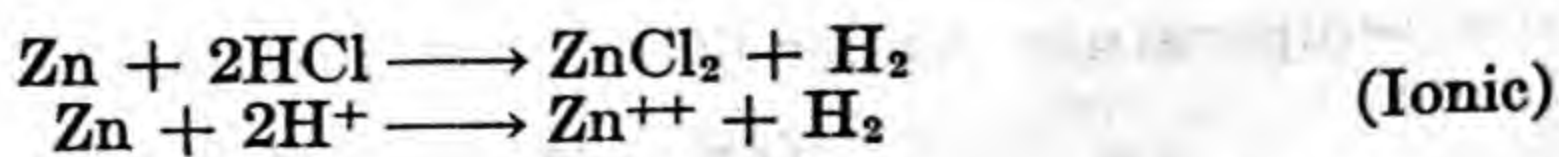
Physical properties. Zinc usually has a dull gray surface which is due to a thin layer of zinc oxide or of zinc carbonate on the metal. The metal can be highly polished, but it soon turns gray again when exposed to the air. Zinc is crystalline and somewhat brittle at ordinary temperatures, but at 100° to 150°C. it is malleable and can be rolled into sheets. Its melting point is relatively low: 419°C.

Uses. Zinc is used chiefly in galvanizing iron and in the manufacture of brass, which is an alloy of copper and zinc. It is used also in the manufacture of batteries, and in the preparation of zinc oxide and zinc sulfide, which are used as white pigments. Galvanized iron is sheet iron which has been cleaned thoroughly by "pickling" in dilute sulfuric acid, and then dipped in a vat of molten zinc. A thin layer of zinc adheres to the surface of the iron.

A method of galvanizing iron by electroplating is rapidly gaining in importance, especially in the manufacture of wire screens and automobile parts. By this method the thickness of the layer may be varied at will, and the zinc is very firmly attached to the iron or steel.

Sherardized iron is produced by heating iron objects with zinc dust in a revolving drum. This method is used for galvanizing articles like pulleys and bolts. Another process consists in spraying very fine zinc dust with tremendous force against the iron which is to be covered. The zinc adheres to the surface of the iron.

Chemical properties. In the presence of moist air, zinc forms a basic carbonate, a thin layer of which acts as a protective coating and prevents further corrosion. When heated to a high temperature, molten zinc combines very readily with oxygen of the air, forming zinc oxide. Zinc reacts with hydrochloric acid, liberating hydrogen:

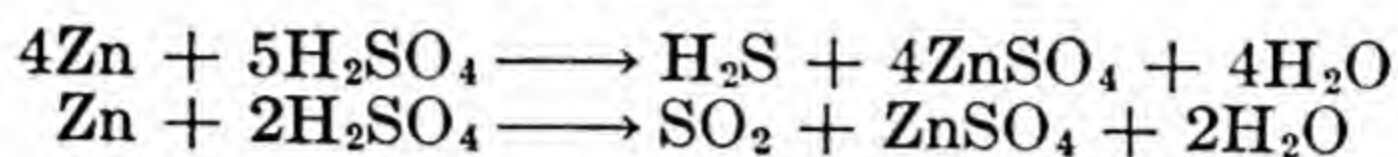


The products formed when zinc acts upon sulfuric acid or nitric acid depend upon the concentration of the acid and the

temperature of the reaction. With dilute sulfuric acid, hydrogen is formed:

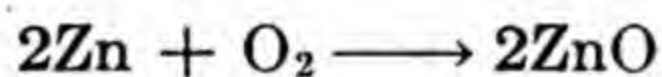


With a more concentrated solution of the acid, either hydrogen sulfide or sulfur dioxide is formed:



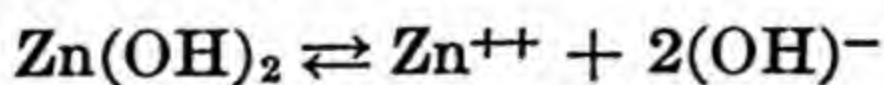
The equations for the reactions of zinc with nitric acid have been given (see page 270).

Compounds. The most important compound of zinc is zinc oxide. It is used in the manufacture of white paint and also in the preparation of rubber for automobile tires. The two principal pigments used in white paint are white lead and zinc oxide. In some countries the use of white lead is prohibited by law because of its poisonous effect upon workmen. Zinc oxide is more expensive than white lead, but it has the advantage of not turning black in the presence of hydrogen sulfide or other sulfur compounds. Small quantities of sulfur compounds are present in the gas burned in kitchen stoves. A lead paint is not satisfactory for interior use, since it reacts with sulfur compounds to form lead sulfide, which is black. Zinc sulfide, like the oxide, is white. Pure zinc oxide is manufactured by heating the metal in air:

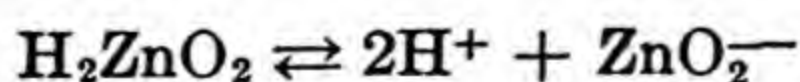


The formation of zinc oxide, when compounds of zinc are heated in air, serves as a test for this element. If a mineral or compound containing zinc is heated with a blowpipe on a block of charcoal, zinc oxide is formed. This oxide is volatile and spreads over the surface of the charcoal. When hot, the zinc oxide is yellow, but it turns white upon cooling.

Zinc hydroxide is an amphoteric compound. In the presence of a strong acid an amphoteric substance acts like a base, and in the presence of a strong base it acts like an acid. The formula of zinc hydroxide may be written $\text{Zn}(\text{OH})_2$ or H_2ZnO_2 , and its capacity to act either as an acid or a base is explained by the fact that it can ionize in two ways:



and



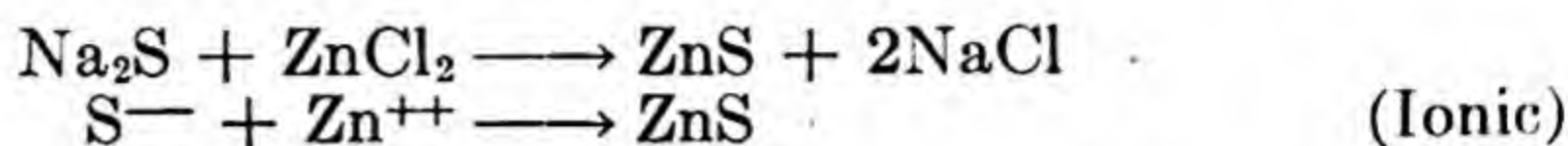
Zinc hydroxide neutralizes hydrochloric acid, forming zinc chloride:



It neutralizes sodium hydroxide, forming sodium zincate:



Zinc sulfide. A white salt having the formula ZnS is made by adding a soluble sulfide to a solution of a zinc salt:



Zinc sulfide dissolves in acids, forming hydrogen sulfide:



When hydrogen sulfide is added to a soluble zinc salt *in neutral or alkaline solution*, zinc sulfide is precipitated. Zinc sulfide cannot be precipitated in an acid solution, for it is soluble in acids.

Zinc sulfide is sometimes used alone as a pigment, but more often it is mixed with barium sulfate. Both of these salts are white and insoluble. This mixture is known as *lithopone*. The manufacture of lithopone was discussed in the chapter on the alkaline earth metals (see page 359).

Zinc chloride is made by dissolving zinc in hydrochloric acid and evaporating the solution. It is a deliquescent salt; that is, it takes up water from the air. Solutions of it have the ability to dissolve oxides of some metals, and it is useful, therefore, as a flux in the process of soldering to keep metallic surfaces clean. It is used extensively in the preservation of wood, as a fungicide, and as an insecticide. Railroad ties to be used in warm climates are treated with a solution of zinc chloride to stop the growth of fungi and to prevent termites (white ants) from destroying the wood. The chloride leaches out of the wood in time.

Questions and Exercises

1. How is zinc oxide made (a) from zinc carbonate, (b) from zinc sulfide?
2. How is metallic zinc obtained from zinc oxide?
3. What is galvanized iron? How is it made?
4. What is brass?
5. What products are formed when zinc reacts with the following compounds: (a) hydrochloric acid, (b) dilute sulfuric acid, (c) concentrated sulfuric acid, (d) nitric acid, (e) copper sulfate solution?
6. Under what condition does zinc hydroxide act like an acid?
7. When does zinc hydroxide act like a base?
8. What is an amphoteric substance?
9. Zinc sulfide and oxygen were heated together in a closed vessel. Did the gas pressure in the vessel increase, decrease, or remain constant after the reaction started?

10. If a solution of sodium hydroxide is added to one of zinc chloride, a precipitate is formed which dissolves upon further addition of sodium hydroxide. Explain. Write equations for the reaction which occurs (a) when the precipitate is formed and (b) when the precipitate dissolves.

11. How many grams of hydrogen are produced when 650 g. of zinc react with an excess of sulfuric acid?

12. How many liters of hydrogen, measured under standard conditions, are formed when 650 g. of zinc react with an excess of dilute sulfuric acid?

PART 2

Cadmium and Mercury

Cadmium

Cadmium closely resembles zinc. It is found with zinc in its ores, but the amount is usually less than 1 per cent. In some silicates cadmium is found to the extent of 3 per cent or more.

Extraction from its ores. Cadmium is more easily reduced than zinc, and the ores of the two metals are usually treated together. The ores are roasted (heated with air) to convert the sulfides to oxides, and the oxides are then reduced by heating with carbon. Cadmium can be separated from zinc by boiling the liquids. Zinc boils at 907°C . and cadmium boils at 767°C . Cadmium, therefore, can be distilled from the zinc, or it can be separated from zinc electrolytically.

Properties and uses. Cadmium is a white metal, much like zinc in appearance and properties. It is slightly harder than zinc and corrodes less readily. For this reason it makes a better material with which to galvanize, or plate, iron and steel. Automobile brake parts which are exposed to much moisture and heat are plated with cadmium to prevent corrosion. Some tools and rustproof wire are made of steel plated with cadmium. Cadmium is contained in many alloys. Copper containing 1 per cent of cadmium is considerably harder and has greater tensile strength than pure copper, while its conductivity is only slightly reduced. This fact has proved of great value in long-distance transmission lines.

Cadmium is also used in alloys designed for use as bearings. More than half of the cadmium produced in the United States is used in automobile bearings.

Compounds. Cadmium compounds are all similar to those of zinc. Cadmium hydroxide, however, is not amphoteric. Cadmium, being toward the bottom of the group, is a more strongly metallic element than is zinc. Cadmium sulfide is a bright yellow solid which is formed when hydrogen sulfide is added to a solution of cadmium salt. It is known as "cadmium yellow," an expensive pigment used mainly by artists.

Mercury

Mercury was known at least as early as 400 B.C. It was called liquid silver, or quicksilver.

Occurrence. Mercury is sometimes found in nature in the form of small globules scattered through rocks. It is found principally as cinnabar, a red sulfide of mercury, having the formula HgS .

Spain and Italy are the largest producers of mercury. The United States comes third on the list, with an annual production of more than 1,000,000 lb., most of which comes from California, Oregon, Arizona, Nevada, Arkansas, Texas, and Washington.

To obtain free mercury from the sulfide, the ore is heated with a limited amount of air. Sulfur dioxide and mercury are formed. Both are gases at the temperature of the furnace, but the mercury condenses to the liquid state when the mixed gases are cooled.



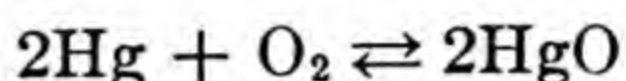
Physical properties. Mercury is a heavy metallic liquid. It is one of the two elements which exist in the liquid state under ordinary conditions, the other liquid element being bromine. Mercury freezes at -40°C . and boils at 357°C . It is a good conductor of electricity. Mercury vapor is poisonous.

Uses. Mercury is used in the manufacture of thermometers, because changes in temperature cause more uniform changes in the volume of mercury than in almost any other liquid. It is used also in barometers and mercury-arc lamps. It is used to some extent in the recovery of free gold from ores, and in the manufacture of mercury fulminate, an organic compound which is used as a detonator. The attractive red pigment called cinnabar or vermilion is used in some paints. The blue and green neon signs used for advertising are demanding more mercury every year. Large quantities of mercury are used in making drugs.

Amalgams. Mercury dissolves gold, silver, tin, copper, zinc, and a number of other metals. These solutions, known as *amalgams*, may be either liquids or solids. The amalgams of gold, silver, tin, and cadmium are used in dentistry. A freshly prepared mixture of powdered gold or silver and mercury is capable of being molded to fill a tooth cavity. After a short time the amalgam becomes solid and hard. In the metallurgy of gold the crushed ore is floated over mercury and the free gold dissolves in the mercury, forming an amalgam. The gold is recovered by distilling off the mercury.

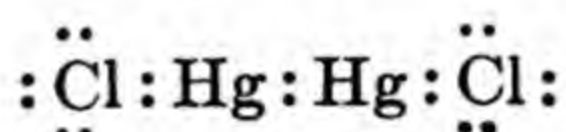
Sodium and potassium form amalgams when dissolved in mercury. These are often used in the laboratory in place of the alkali metals themselves because they are less reactive.

Chemical properties. Mercury does not dissolve in hydrochloric acid or in dilute sulfuric acid, but it does dissolve in nitric acid and concentrated sulfuric acid. The reactions are similar to those of copper and silver. Mercury combines with oxygen when heated, but at a higher temperature the red oxide decomposes:



Compounds. Mercury forms two types of compounds: *mercurous* compounds, and *mercuric* compounds.

Mercurous chloride, Hg_2Cl_2 , known as *calomel*, is a colorless insoluble salt. The atoms are combined as shown in the following formula:



The mercurous ion, therefore, is Hg_2^{++} .

Mercuric chloride, HgCl_2 , known as *corrosive sublimate*, or bichloride of mercury, unlike mercurous chloride, is a violent poison. It can be sublimed (that is, vaporized without melting). It is prepared by heating a mixture of mercuric sulfate and sodium chloride. Mercuric chloride distills out of the mixture and condenses to a solid on cooling:



Mercuric chloride does not behave like other salts in solution. Instead of being completely dissociated into its ions, like NaCl , it is dissociated only to a very small extent. A solution of HgCl_2 contains only small amounts of Hg^{++} and Cl^- ions.

Because of its poisonous property, a very dilute solution is used in surgery for sterilizing instruments and cleansing wounds. It is used also in preserving wood and in embalming.

Mercuric sulfide, HgS , used by artists as a red paint, is known as *vermilion*. When precipitated from solution, mercuric sulfide is black, but it may be converted into the red form by heating. It is used to color sealing wax, rubber, and lipstick.

Mercuric thiocyanate, $\text{Hg}(\text{CNS})_2$, is an insoluble salt made from a solution of sodium thiocyanate, NaCNS , by the addition of a soluble mercuric salt. A paste made of mercuric thiocyanate, water, and some binding material, such as gum arabic, is molded into cones, then dried, and sold as "Pharaoh's Serpents." When ignited, the mixture burns slowly and the ash spreads out in serpentlike forms.

Questions and Exercises

1. Describe cadmium, and mention one use for the metal.
2. Describe mercury, and explain the process of obtaining it from cinnabar.
3. Specify three uses of mercury.
4. What is an amalgam?
5. What is (a) calomel and (b) corrosive sublimate?
6. Write an equation for the reaction that occurs when cadmium sulfide is heated in air.
7. The density of mercury is 13.6 g. per cubic centimeter. What is the weight of 1 liter of mercury? What is the volume of 1000 g. of mercury? What is the weight in pounds of a liter of mercury?
8. Calculate the weight of sulfur in 1 lb. of mercuric thiocyanate.
9. Write an equation for the reaction that would occur if a solution of common salt were added to a solution of mercurous nitrate, $\text{Hg}_2(\text{NO}_3)_2$. Is one of the products of this reaction insoluble?
10. Why are mercury thermometers not used in the arctic regions?
11. Why is alcohol used to sterilize mouth thermometers, rather than (a) a solution of mercuric chloride, (b) boiling water?
12. How do the atoms of the second subgroup differ from the atoms of the second main group of the periodic system? In what ways are they alike?

UNIT XV

Electromotive Series; Electric Cells; Storage Batteries; Electrolysis; Electrode Potentials

PART 1

The Electromotive Series

In our study of the chemical properties of many of the metallic elements, we learned that there are two classes of metals: (1) those that displace hydrogen ions from dilute acids, forming hydrogen gas and the corresponding salt of the metal; (2) those that do not displace hydrogen ions, but require an oxidizing acid, such as concentrated sulfuric acid or nitric acid, for their solution. In the first class are the metals of Group I: lithium, sodium, potassium, rubidium, and cesium; the metals of Group II: beryllium, magnesium, calcium, barium, strontium, and radium; the first two metals in the subgroup of Group II: zinc and cadmium; and the metals of Group III, headed by boron and aluminum. The metals studied thus far which belong to the second class are copper, silver, gold, and mercury. These all belong to subgroups of Group I and Group II.

There are differences in the tendencies of elements to give up valence electrons and to become ions. The metals which react with dilute acids, and hence with hydrogen ions, have a greater tendency than has hydrogen to give up electrons and to exist in the form of ions. For example, when an element like sodium is placed in a solution of an acid such as hydrochloric acid, the sodium atoms give up their valence electrons to hydrogen ions with such rapidity that an explosion usually occurs:



The hydrogen atoms which have received electrons from sodium atoms unite in pairs to form molecules of hydrogen gas, which escapes from the solution. We usually say that the sodium has replaced the hydrogen in the solution.

In like manner, when we pour a dilute acid on zinc, since zinc has a greater tendency to give up valence electrons than has hydrogen, two hydrogen ions receive two electrons from each zinc atom. In this process hydrogen gas is formed, and zinc goes into solution as ions:



A metal like copper, on the other hand, has less tendency than hydrogen to give up valence electrons. If dilute sulfuric acid is poured onto some metallic copper, no reaction takes place. Copper atoms do not yield their valence electrons to hydrogen; hence the hydrogen remains in the form of ions in the solution, and we say that copper does not react with, or dissolve in, dilute acids.

Just as there is a difference between the metals and hydrogen, in tendencies to give up electrons, so is there a difference between the metals themselves in tendencies to yield electrons. If a strip of zinc is immersed in a solution of a copper salt (this means actually placing it in contact with copper ions), the strip of zinc gradually disappears. At the same time the blue color which is due to copper ions gradually fades and metallic copper appears on the zinc strip. Zinc atoms have given their valence electrons to copper ions, and thus have converted the copper ions into copper atoms. The zinc atoms at the same time become zinc ions:



When a strip of copper is placed in a solution containing zinc ions, no change takes place, because copper holds its two electrons more firmly than zinc does.

If, however, a strip of copper is placed in a solution of silver nitrate, the solution gradually turns blue, owing to the formation of copper ions. The copper strip gets smaller and smaller, and metallic silver precipitates:



Again we find that the reverse action does not take place.

Similarly, a strip of magnesium dissolves in a solution of a zinc salt, and metallic zinc precipitates or plates out on the magnesium.

The relative tendencies of metals to give up valence electrons have been determined in the laboratory, and the metals can

be arranged in the order of this tendency to yield electrons. Such an arrangement of the elements is known as the *electromotive series* or the *replacement series*. In the accompanying table some of the common elements are arranged in the order of their tendency to yield electrons. The metals at the top of the list are very reactive, and they are not easily obtained in the free state. Those near the bottom of the list are not very reactive. They do not tarnish or corrode easily, and they are found in the free state in nature. Elements at the top of the list give up electrons easily. Those at the end of the list hold electrons more firmly. A metal will displace any other metal that occupies a lower position in the list. For example, if calcium metal were placed in a solution containing the ions of any one of the elements beneath it in the table, the calcium would dissolve and become calcium ions and the other element would plate out or precipitate in the metallic state.

THE
ELECTROMOTIVE
SERIES

<i>Element</i>	<i>Ion</i>
K	K ⁺
Na	Na ⁺
Ca	Ca ⁺⁺
Mg	Mg ⁺⁺
Al	Al ⁺⁺⁺
Zn	Zn ⁺⁺
Fe	Fe ⁺⁺
Ni	Ni ⁺⁺
Cd	Cd ⁺⁺
Sn	Sn ⁺⁺
Pb	Pb ⁺⁺
<hr/>	
H ₂	H ⁺
<hr/>	
Cu	Cu ⁺⁺
Hg	Hg ⁺⁺
Ag	Ag ⁺
Au	Au ⁺⁺⁺

The tendency of any metal to hold electrons is less than that of any metal below it in this table. Although hydrogen is not a metal, it is included here, for the table shows which of the metals will liberate hydrogen from an acid. Any metal above hydrogen in the table will liberate hydrogen from an acid, but a metal below hydrogen will not do so. Aluminum, for example, reacts with hydrochloric acid (H⁺ in the table), yielding aluminum ions Al⁺⁺⁺, and hydrogen gas, H₂; while copper, mercury, silver, and gold will not liberate hydrogen from an acid, and hence do not dissolve in dilute acids.

The two columns in the electromotive series constitute partial lists of the common oxidizing and reducing agents. The positive ions are oxidizing agents. They are capable of removing electrons from atoms or groups that are susceptible to oxidation. *Removal of electrons is oxidation.* The free metals—the left-hand column—are reducing agents. They are capable of yielding electrons to other atoms. *Addition of electrons to an atom or group is reduction.*

We could make these lists of oxidizing and reducing agents more complete by adding nonmetals. Chlorine, bromine, and iodine are good oxidizing agents, and they could be placed in the right-hand column. The corresponding ions Cl⁻, Br⁻, and I⁻ would be placed opposite them in the column of reducing agents.

Questions and Exercises

1. How are the elements arranged in the electromotive series?
2. Which of the following elements gives up electrons most readily: (a) zinc, (b) magnesium, (c) iron?
3. Write an equation for the reaction, if one occurs, when (a) a strip of iron is placed in a solution of cadmium sulfate; (b) zinc metal is placed in a solution of ferric chloride; (c) gold is placed in a solution of a silver salt; (d) silver is placed in a solution of a gold salt; (e) tin is placed in dilute hydrochloric acid; (f) copper is placed in dilute sodium chloride solution.
4. Explain in terms of the atom's tendency to hold electrons why hydrochloric acid dissolves zinc and not mercury.
5. A piece of aluminum is placed in a solution of copper sulfate and allowed to stand for several days. Predict the result.
6. A piece of copper is placed in a solution of aluminum sulfate and allowed to stand for several days. Predict the result.
7. A piece of zinc is electrically neutral. When placed in a dilute acid solution, some of it immediately goes into solution as zinc ions, Zn^{++} . Is the undissolved portion then neutral or electrically charged?
8. Define oxidation.
9. Define reduction.
10. Which atom or ion is oxidized and which is reduced when zinc dissolves in an acid? The equation is:



PART 2

Electric Cells

Wet cells. When electrons are transferred from zinc atoms to copper ions, as indicated by the equation on page 405, a certain amount of chemical energy is set free in the form of heat. If the electrons were not allowed to go from zinc atoms to copper ions directly, but were made to pass through an electric motor or an

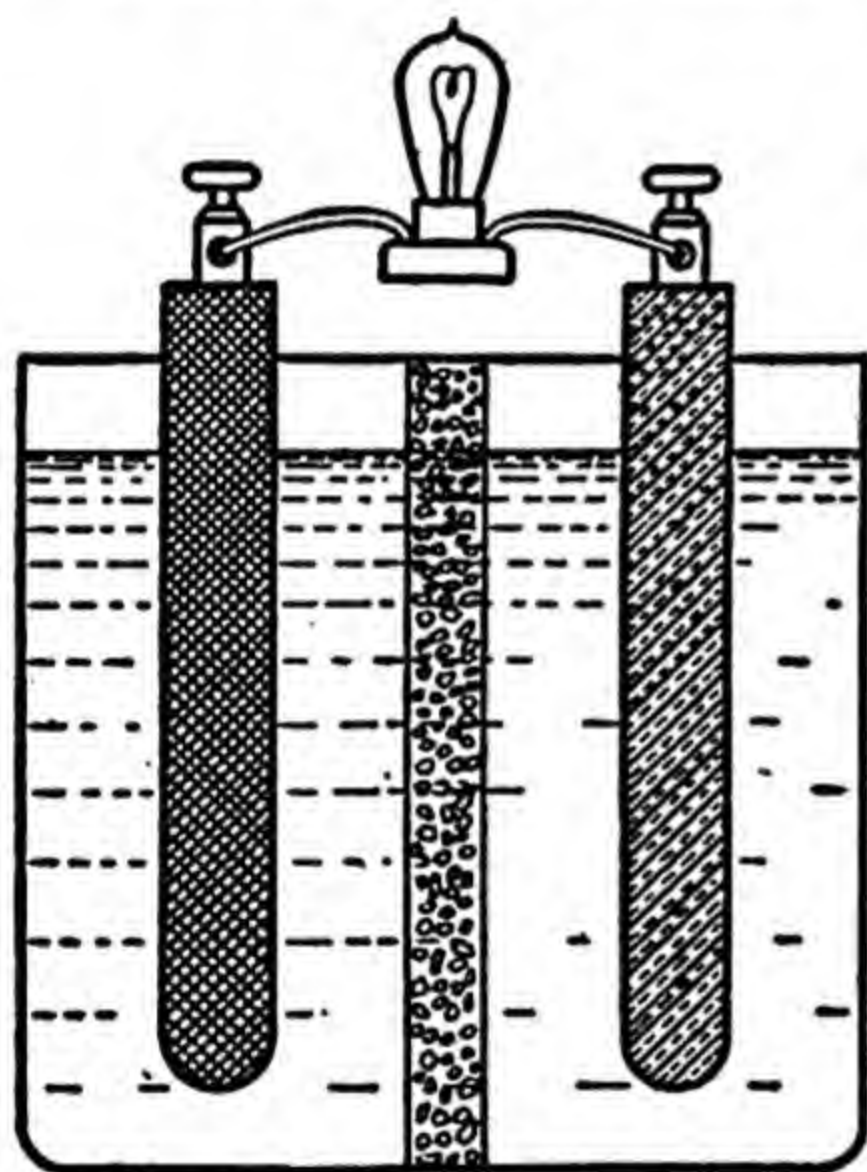
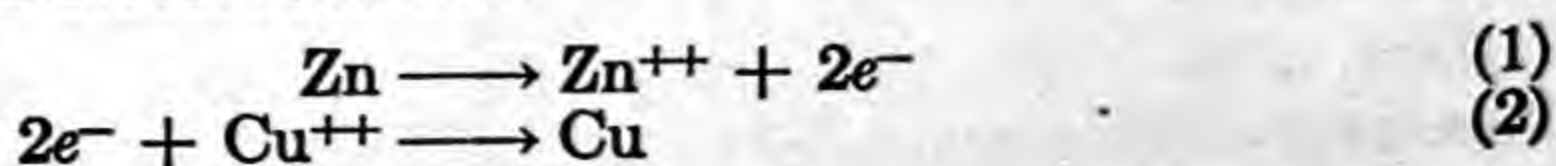


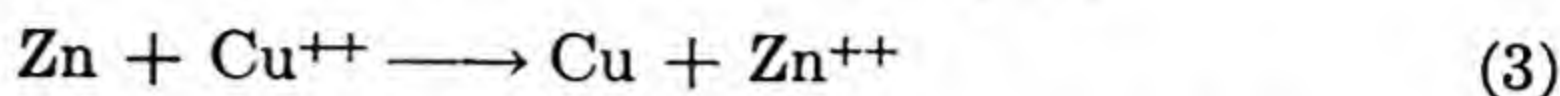
Fig. 164. A wet cell.

electric light bulb on the way, most of the energy could be made to do useful work instead of heating the solution. This application is what the wet battery accomplishes. The wet cell is divided into two compartments by means of a porous wall through which ions can flow but which prevents the mixing of the solutions by stirring. In one compartment is placed a solution of zinc sulfate, and in the other, copper sulfate. A piece of zinc is placed in the zinc sulfate, and a piece of copper in the copper sulfate solution. These metal strips or rods constitute the electrodes of the cell. Since the zinc atoms give off electrons more readily than the copper

atoms do, some zinc ions leave the zinc electrode and pass into solution, leaving their valence electrons on the electrode. These electrons distribute themselves throughout the zinc electrode, and if this electrode is connected to the copper electrode by a conductor, the electrons flow through the conductor into the copper. The electrons which come to the surface of the copper are taken up by Cu^{++} ions from the copper sulfate solution which is in contact with the electrode. In this way copper atoms are formed from the ions, and these atoms plate out on the copper electrode. The reactions at the two electrodes are:



The total reaction (the sum of reactions 1 and 2) is:



The reaction is represented graphically by Fig. 165. This reaction is the same one that takes place when a piece of zinc dissolves in a solution of copper sulfate, but in one case heat is evolved and in the other case the electrons are made to pass through a conductor, and the energy of the reaction appears in the form of electricity instead of heat.



Fig. 165.

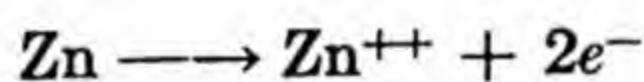
The Daniell cell. In practice, a porous cup instead of a straight porous wall is used. The cup is placed inside a jar with one electrode inside the porous cup and one outside. Such a cell with copper and zinc as electrodes is called a *Daniell cell*. Sulfuric acid is often used in place of the zinc sulfate solution. Zinc ions are not necessary, since they are formed and not used up in the cell.

The porous wall in the cell prevents the Cu^{++} ions from coming in contact with the zinc electrode. If such contact were permitted, the Cu^{++} ions would take electrons directly from the zinc, and the copper atoms formed in this way would plate out on the zinc, eventually covering it with a layer of copper. The result would be two copper electrodes, and the flow of electricity would cease. The Zn^{++} ions flow through the porous wall by electrical attraction into the copper sulfate solution, but there they have no effect. Zinc ions cannot react with metallic copper, but copper ions can react with metallic zinc. Copper ions take electrons away from zinc atoms, as shown in equation 3, above.

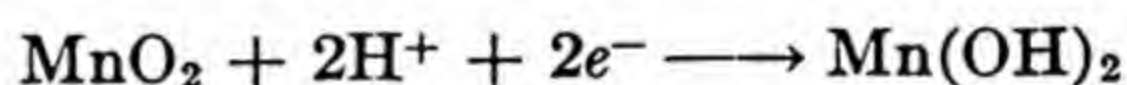
Such an arrangement is known as a primary cell or *voltaic cell*. Any simple replacement reaction can be made into such a cell. One electrode always consists of a substance that has a greater tendency to give up electrons than the substance composing the second electrode. The first electrode therefore gives up electrons, which pass through a wire and thus reach the ions of the second substance in which the electrode is immersed. The substance that gives up electrons is said to be *oxidized*; that which receives electrons is said to be *reduced*. The farther apart the metals are in the electromotive series, the greater is the electromotive force, or the voltage, of the cell. The first metals in the

electromotive series are often called *electropositive* elements because they readily form positive ions, but the process of passing into solution as positive ions leaves the undissolved residue of the metal with extra electrons. On this account the so-called electropositive elements are the ones that deliver electrons to a conductor.

The dry cell. A convenient cell for use where a small current is required, especially when it is not to be used continuously, is the dry cell. The name is misleading, because the cell contains water which is essential to its operation. The electrodes and electrolyte are contained in a can which is sealed at the top with resin, so that the contents of the can are not disturbed during rough handling. The box or can is made of zinc, which acts as one electrode. There is a carbon rod in the center, and the interior is filled with ammonium chloride, manganese dioxide, and moistened sawdust, the sawdust acting as a filler and giving a porous texture to the mixture. The ammonium chloride hydrolyzes to give hydrogen ions and ammonium hydroxide. At the zinc electrode, zinc ions enter the solution in the moist sawdust and leave the electrons behind on the zinc electrode:



When the battery is connected, these electrons flow from the zinc through the connecting wire to the carbon rod and from there into the manganese dioxide. Here they combine with the MnO_2 and with hydrogen ions supplied by the ammonium chloride:



The two reactions given here do not represent all the chemical changes that occur in a dry cell, but they indicate the main processes which lead to a flow of electrons through the external circuit. A dry cell deteriorates as the ammonium chloride and zinc electrode are used up. We have all observed the wetness of a worn-out flashlight battery. The can becomes porous as the zinc is gradually converted into zinc chloride, and zinc chloride is deliquescent.

Questions and Exercises

1. A battery is made by immersing a piece of zinc in a solution of zinc sulfate and a piece of copper in a solution of copper sulfate. The two solutions are separated by a porous porcelain wall, and the two metals are connected above the solutions by a wire. In which direction do electrons travel through the wire?

2. A cell is made by placing a bar of iron in a solution of an iron salt on one side of a porous partition and a bar of silver in a silver nitrate solution on the opposite side of the partition. The two metal bars are connected by means of a

wire above the solutions. Which metal will dissolve? In which direction will electrons flow through the wire? Will the voltage of this cell be greater or less than that of the Daniell cell?

3. Would a voltaic cell containing magnesium and gold electrodes be as efficient as one containing zinc and copper?

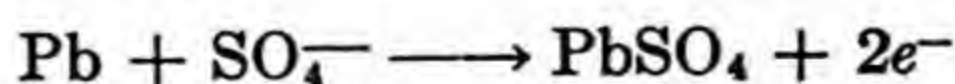
4. Theoretically, which metals should give the highest voltage? Why are these metals not used?

PART 3

Storage Batteries

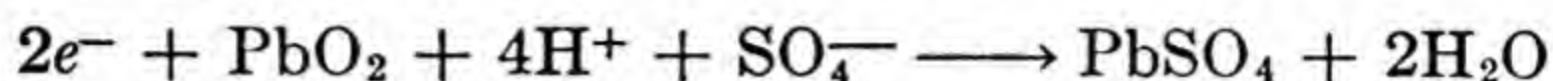
The reaction that takes place in a storage battery is one which goes easily in either direction; that is, it is a reversible reaction. When electricity is passed through the cell from an outside source, a chemical reaction takes place which changes the character of the electrodes. When the outside source of electricity is removed, the reverse reaction takes place in the cell with an accompanying flow of electricity.

The lead storage battery. The most familiar type of storage cell is the lead storage battery. It is used in automobiles for supplying current to the starter, lights, and spark plugs, and it is also used in some radios. In its simplest form a storage battery consists of a plate of lead and one of lead dioxide immersed in sulfuric acid. To obtain greater capacity, several pairs of plates may be placed in each cell of a battery. The plates are lead grids. In one set the grids are filled with spongy metallic lead, and in the other set the filling material is lead dioxide. Neither lead nor lead dioxide acts upon sulfuric acid at an appreciable rate unless the two plates are connected through a metallic conductor of electricity. When the plates are connected by a wire, a chemical reaction takes place at each plate and the energy derived from these reactions appears mainly in the form of electrical energy. A current of electricity flows through the connecting wire. When the battery is discharging (terminals connected), lead ions, Pb^{++} , escape from the surface of the lead plate, leaving electrons behind. Most of the lead ions do not actually enter the solution, because they react immediately with sulfate, SO_4^- , ions already present in the solution and in contact with the lead plate. Insoluble lead sulfate is formed on the surface of the plate. The reaction taking place at the lead electrode is:

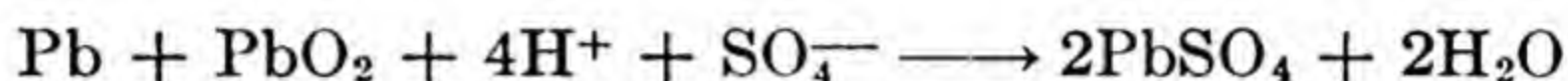


The electrons released in the lead electrode flow through the circuit and enter the lead dioxide electrode. There they enter the valence shells of lead atoms, changing the valence from 4 to 2.

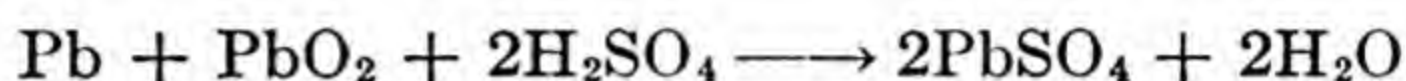
The Pb^{++} thus formed reacts with sulfate ion, forming insoluble PbSO_4 . Hydrogen ions from the sulfuric acid react with the oxygen, released from the lead dioxide, to form water. The total reaction taking place at the lead dioxide electrode is:



The whole cell reaction, including both electrodes, is the sum of the last two equations:



or



When completely discharged, both plates are coated with lead sulfate, and much of the sulfuric acid has been used in forming lead sulfate and water.

To charge a battery, electrical energy from an independent source is forced through the system in the opposite direction. Connection is made with a generator, or dynamo, the positive terminal of the dynamo being connected with the positive pole of the battery and the negative terminal of the dynamo with the negative pole of the battery. Electrons are thus forced into the negative plate and taken out of the positive plate. The reactions given above for the discharging process are reversed when the battery is being charged, lead sulfate being converted into lead at one electrode, and into lead dioxide at the other. Sulfuric acid is formed at the same time and is restored to the solution.

In an automobile, the battery is normally recharged by means of the generator, which is operated by the engine. Care must be taken that the battery is filled from time to time with distilled water, to replace water lost by evaporation. A storage cell should not be allowed to stand idle for a long period of time, because it discharges slowly and covers the plates with crystalline lead sulfate. Recharging is very difficult in these circumstances.

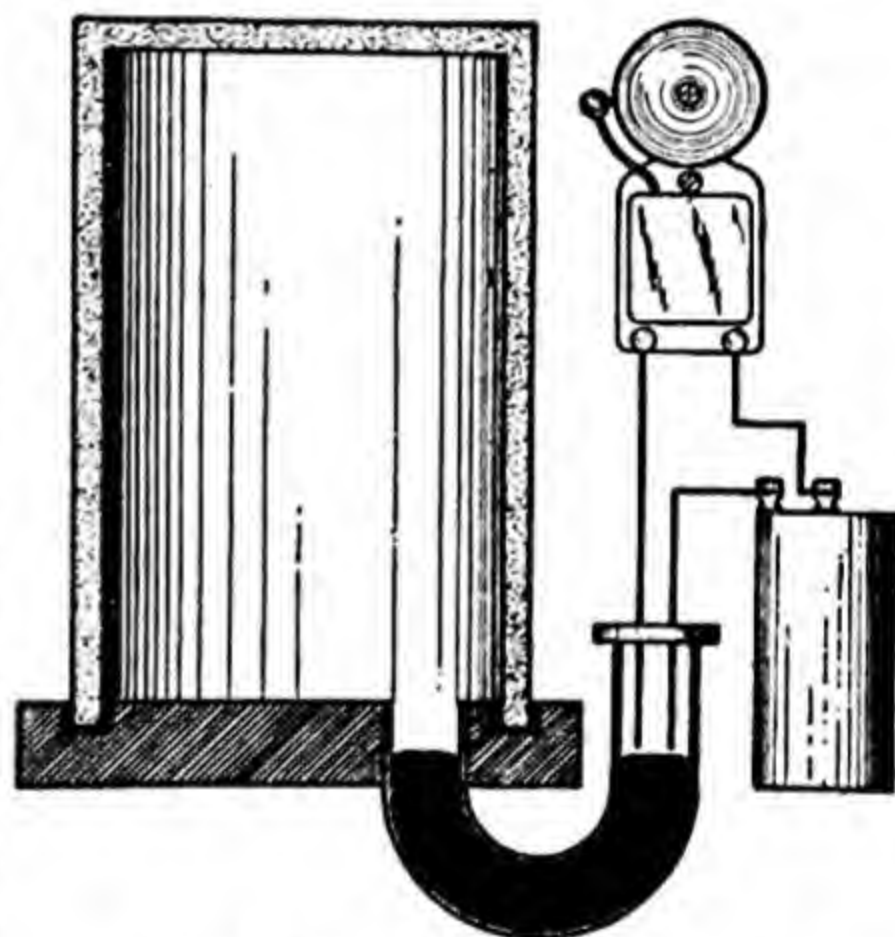
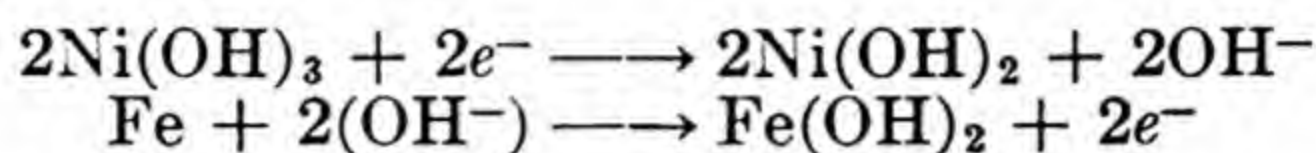


Fig. 166. A hydrogen detector. In the process of charging a battery, some hydrogen is evolved. In submarines and in other poorly ventilated places there is danger of producing an explosive mixture of hydrogen and air. Hydrogen diffuses through the porous walls of the detector faster than air can escape. This added hydrogen creates a pressure in the detector chamber which forces mercury to a higher level in the right side of the U-tube. When the mercury makes contact with the leads from the battery and the bell, a warning signal is given.

The Edison cell. When an Edison cell is fully charged, the positive plate contains Ni(OH)_3 and the negative plate consists of finely divided iron. The electrolyte is a solution of potassium hydroxide and usually a little lithium hydroxide. During discharge, the positive plate changes to Ni(OH)_2 , and the negative to Fe(OH)_2 .

The reactions that take place at each electrode are represented by the following equations:



During the charging process the reactions go from right to left.

The advantage of the Edison battery is that it suffers no damage from disuse. It is more expensive than a lead storage battery, but it has a longer life.

Questions and Exercises

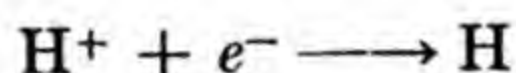
1. What reactions take place at each of the electrodes when a lead storage battery discharges? When it is charged?
2. Assuming that there are 20 million automobiles in the United States and assuming further that the average life of a storage cell is three years, estimate very roughly the amount of lead consumed annually in the production of storage batteries. The average storage cell contains about 20 lb. of lead.
3. What reactions take place at each electrode in the Edison cell when it is discharging? When it is being charged?
4. What advantages has the Edison cell over the lead storage cell? What disadvantage?
5. Why are storage cells more advantageous than ordinary dry cells for use in an automobile?

PART 4

Electrolysis

When a solution is electrolyzed, some substance becomes oxidized (loses electrons) at the anode, while another substance is reduced (gains electrons) at the cathode. If one faraday of electricity passes through the cell, one equivalent weight of an element is oxidized at the anode and one equivalent weight of another element is reduced at the cathode. A faraday is approximately 96,500 coulombs, or ampere-seconds, of electricity.

Electrolysis of hydrochloric acid. Let us see what happens when a platinum cathode and a graphite anode of a battery are immersed in a solution of hydrochloric acid. Since hydrogen ions are positively charged, they migrate toward the cathode through the solution. Those which come in contact with the electrode acquire electrons—one electron for each ion—and each hydrogen ion which acquires an electron becomes an atom of hydrogen. The reaction at the cathode may be written as follows:



Since hydrogen escapes in the form of molecules, H_2 , we shall write the electrode reaction in the form:



The solution remains electrically neutral at all times, for chloride ions leave the solution at the same rate at which hydrogen ions do. The chloride ions are negatively charged, and they migrate toward the positive electrode—the anode. Each chloride ion which leaves the solution at the anode deposits upon the anode one electron. The reaction at the anode is represented by the following equation:



When one faraday of electricity has been used in the process of electrolysis, 1 g. of hydrogen has been liberated at the cathode and 35.5 g. of chlorine at the anode. The reaction represented by

the whole electric cell is the sum of the two electrode reactions (1) and (2):

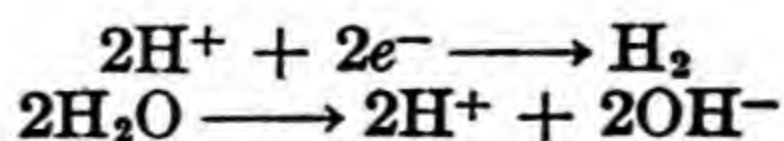


Electrolysis of sodium chloride. A solution of sodium chloride is electrolyzed in the commercial preparation of chlorine and of sodium hydroxide. The products formed at the two electrodes are hydrogen and chlorine, while the sodium ion remains in the solution. On evaporation of the water in the solution, sodium hydroxide is obtained. What is the source of the hydrogen gas and of the hydroxide ions in this process?

The electromotive series of the elements, which we have already studied, shows us that some substances have a greater tendency than others to give up electrons and become ions. The metals, like sodium, at the head of the list give up valence electrons with great ease. Those near the center of the series give them up less readily, while those at the bottom of the list have the least tendency to part with their valence electrons. Conversely, if we supply electrons to the ions of a salt by means of an electrode in an electrolytic cell, the ions of the metals at the bottom of the list tend to acquire electrons more readily than those near or at the top of the series.

In a solution of sodium chloride in water, we actually have four ions present: sodium ions and chloride ions from the salt, and hydrogen and hydroxide ions from the water. There is approximately 0.0000001 mole of hydrogen and the same concentration of hydroxide ions in a liter of water; that is, 10^{-7} mole of each. This quantity appears to be a very small number of ions, but if we recall that there are 6×10^{23} molecules in 1 mole of water, we see that there are approximately 60,000,000,000,000,000 hydrogen ions and the same number of hydroxide ions in one liter. These hydrogen ions migrate with the sodium ions toward the negative electrode. Hydrogen is below sodium in the electromotive series, which means that hydrogen ions have a greater tendency to acquire electrons than have sodium ions. Hydrogen gas, therefore, is formed at the cathode—1 g. for each faraday of electricity—and sodium ions remain, unchanged, in the solution.

As hydrogen ions are used up, more water molecules dissociate into hydrogen and hydroxide ions. The cathode reaction then becomes

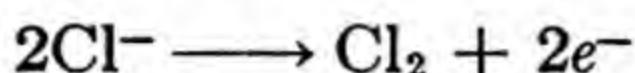


Adding the two equations, we have



We see that water is the only substance used up at the cathode.

Both chloride ions and hydroxide ions migrate toward the anode. Chloride ions have a greater tendency to give up acquired valence electrons than have hydroxide ions. Hence the anode reaction is expressed by the equation

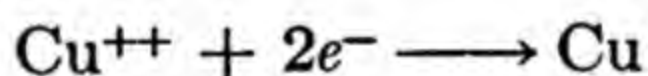


The hydroxide ions remain in the solution. They combine with sodium ions to form sodium hydroxide when the remaining water is evaporated.

Electrolysis of copper sulfate. A solution of copper sulfate also contains several ions—copper ions, sulfate ions, hydrogen ions, and hydroxide ions. If such a solution is electrolyzed, using inert electrodes, metallic copper plates out on the cathode, while oxygen is liberated at the anode.

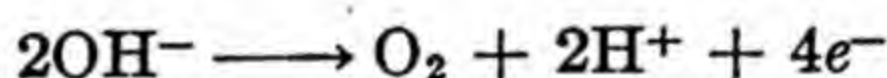
Since copper is below hydrogen in the electromotive series, copper ions acquire electrons first.

Cathode reaction:

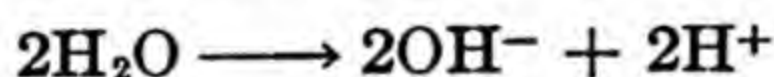


The sulfate ion clings to its electrons more firmly than a hydroxide ion does. Hence the hydroxide ions give electrons to the anode.

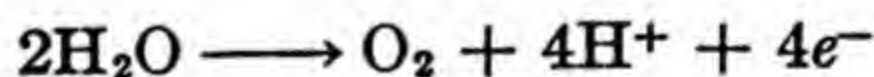
Anode reaction:



More water dissociates into ions:



The sum of the two reactions at the anode is represented by the equation



We see that water is the substance which is actually used up at the anode, and sulfuric acid remains in the solution after the removal of all the copper ions. One equivalent of copper ($63.6 \div 2 = 31.8$ g.) is liberated at the cathode for each faraday of electricity used. At the same time, one equivalent of oxygen ($16 \div 2 = 8$ g.) is freed at the anode.

A table of electrode potentials enables us to predict with certainty which substance in a mixture will be oxidized first in an electrolytic cell. The substance which will be oxidized is not necessarily one of the ions which has migrated toward the electrode. It may be a component of the mixture which was already in contact with the electrode or even the electrode itself.

A table of electrode potentials of some common elements and ions will be found in the Appendix.

Questions and Exercises

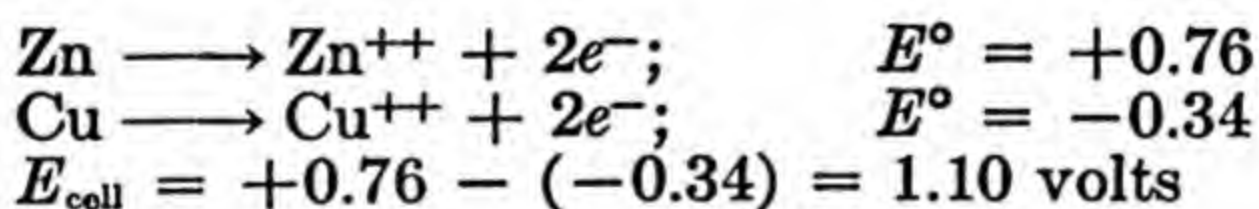
1. Write equations for the electrode reactions in the electrolysis of sodium sulfate.
2. Write equations for the electrode reactions that occur when sulfuric acid is electrolyzed between inert electrodes.

PART 5

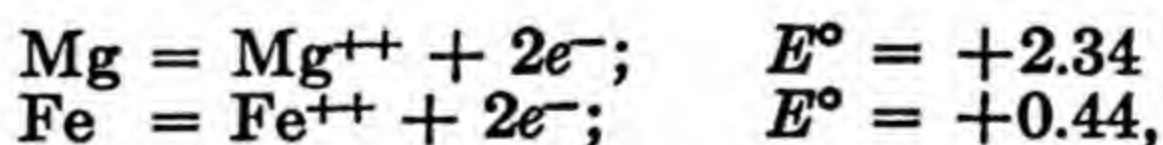
Electrode Potentials

It is impossible to measure the absolute tendency of an element or ion to give up electrons. However, we know that some substances give up electrons more readily than do others. For purposes of comparison, we arbitrarily assign a zero value to the tendency of hydrogen to form hydrogen ions in a molar solution of hydrogen ions. All of the substances in the table on page 514, have been compared with hydrogen in this respect by making each one serve as one electrode in an electric battery, while hydrogen served as the other electrode. The voltage established between the electrodes in each case was measured by means of a voltmeter. In the table on page 514 these voltages are given under E° which is the voltage produced when a metal is immersed in a molar solution of a salt of the metal.

The current which flows through the circuit when any two of the substances are used as electrodes in a battery is easily calculated from these electrode potentials. Thus, a cell composed of a zinc electrode immersed in a dilute (molar) solution of zinc sulfate, and a copper electrode in dilute copper sulfate solution, is the difference between the electrode potentials of these two metals.



Similarly, if the electrodes of a galvanic cell are made of magnesium and iron, immersed in molar solutions of magnesium ions and ferrous ions, respectively, since



the e.m.f. (electromotive force) of the whole cell is $+2.34 - (+0.44) = 1.90$ volts.

When a current is passed through a mixture of substances in an electrolytic cell (electrolysis), the substance present which has the most negative value of E° is oxidized first at the anode.

Questions and Exercises

1. Calculate the voltage of a cell having an aluminum electrode and a silver electrode. Which of the two electrodes in this cell would be the anode?
2. A solution containing sodium chloride and zinc sulfate in water was electrolyzed. Which component of this mixture was first oxidized? Decide which negative ion yields electrons most readily. See page 417.

UNIT XVI

Subgroup IV of the Periodic Table: Germanium, Tin, and Lead

PART 1

Germanium and Tin

We have studied the properties of carbon and silicon, the first two elements of Group IV. We shall now study briefly the properties of two other useful and important members of the same group: tin and lead. Germanium, also a member of this group, is rare and unimportant; it will not be studied in detail.

PHYSICAL PROPERTIES OF GERMANIUM, TIN, AND LEAD

	Ge	Sn	Pb
Atomic number.....	32	50	82
Atomic weight.....	72.6	118.7	207.22
Isotopes.....	70, 72, 73, 74, 76	112, 114, 115, 116, 117, 118, 119, 120, 122, 124	204, 206, 207, 208
Melting point, °C.....	958	231.8	327.5
Boiling point, °C.....	2700	2260	1620
Density, grams per cubic centimeter	5.36	W 7.31 G 5.75	11.34
Electron structure:			
1st shell.....	2	2	2
2nd shell.....	8	8	8
3rd shell.....	18	18	18
4th shell.....	4	18	32
5th shell.....	—	4	18
6th shell.....	—	—	4

Tin

Occurrence. Tin (stannum) is found in comparatively few places in the world. The principal mines are in the Malay States, the Dutch East Indies, Bolivia, Siam, China, and Africa. The United States produces only $\frac{1}{20}$ per cent of the world's supply. Tin was used in prehistoric times. It was mined in England before

the beginning of the Christian era, and after Caesar's conquest of the British Isles it was shipped from there to Rome. The deep, long tunnels that have been excavated in the veins of tin ore in England now extend under the ocean. These old mines are yielding very little tin at the present time.

Tin is found occasionally in the metallic state, but it is usually obtained from its ores. The most important ore containing tin is cassiterite, or stannic oxide, SnO_2 . This is a very heavy mineral which is often found in river beds as heavy gravel known as "stream tin." Much tin is obtained from deposits of this kind, but the ore sometimes occurs in veins and is mined in the usual way.

Extraction from the ore. Tin ore is usually of low grade, being mixed with ores of other metals. It is concentrated by floating off the lighter ores in a stream of water. The heavy tin ore settles from the water in the concentrators. It is then roasted to separate it from such impurities as arsenic and sulfur. Treatment with dilute hydrochloric acid or sulfuric acid removes most of the zinc, iron, copper, and bismuth. The ore is then mixed with anthracite coal in a blast furnace, and is reduced to the metallic state:



The ore is easily reduced, and the free metal melts at a low temperature (231.8°C). It is, therefore, easily freed from the ore and from other metals. These properties account for the fact that tin was one of the first metals used by man.

Some of the tin used at the present time in the United States is recovered from tin plate. The method consists in exposing the cans and utensils to the action of chlorine gas. This changes the tin to stannic chloride, a colorless liquid which boils at 114°C . and which is separated from iron chloride by distillation. The quantity of tin recovered annually in this way in the United States amounts to several thousand tons.

Physical properties. Tin is a silvery-white metal. It is crystalline in structure, and if a bar of tin is bent, the friction between the tiny crystals within the metal gives rise to a peculiar sound, called the "tin cry." Tin is very malleable and may be rolled into thin foil.

Tin exists in several allotropic forms. The ordinary form, as it appears on tin plates, is stable at and above room temperature. Below 18°C . tin has a tendency to change to another form which is a gray powder, and the lower the temperature the greater is the tendency for the change to occur. The transformation takes

place so slowly that ordinary white tin can be kept below the transition temperature for weeks at a time. In 1851 the change was first observed when the tin organ pipes in a church in Germany disintegrated. During the winter of 1867-1868 tin roofing in St. Petersburg became infected with the "tin disease," as it was then called. At low temperatures the change to the gray tin takes place rapidly if the white tin is in contact (seeded) with the gray form. The action resembles that of a supersaturated solution from which the dissolved salt precipitates when the solution is seeded with a crystal.

Tin so successfully resists the action of air, water, and carbonic acid that it is used extensively as a covering for cheaper metals. Tin plate is made by immersing clean sheets of iron in molten tin. A thin layer of tin adheres to the iron, protecting it from oxidation by the air. If the plating is not well done and iron is exposed through pinhole openings in the tin layer, then the iron rusts very rapidly. Iron and tin in contact with water act like a galvanic battery, and iron, preceding tin in the electromotive series, has the greater tendency to go into solution. The dissolved iron is then converted into a carbonate or an oxide of iron. This phenomenon is easily observed in the rusting of a tin can. The can may appear to be quite whole, but it will break to pieces when pressed slightly, showing that the iron between the layers of tin has rusted away. In the case of iron galvanized with zinc, it is not so important to have the covering complete, for in the zinc-iron couple zinc is the element which dissolves. (See Electromotive Series, page 406.)

Pure distilled water is made by condensing water vapor in tin pipes. Gold or silver pipes would serve the same purpose but would be more expensive. Iron, zinc, and glass tubes are too soluble to be used when water of highest purity is required. Many valuable alloys are made by melting together two or more metals.

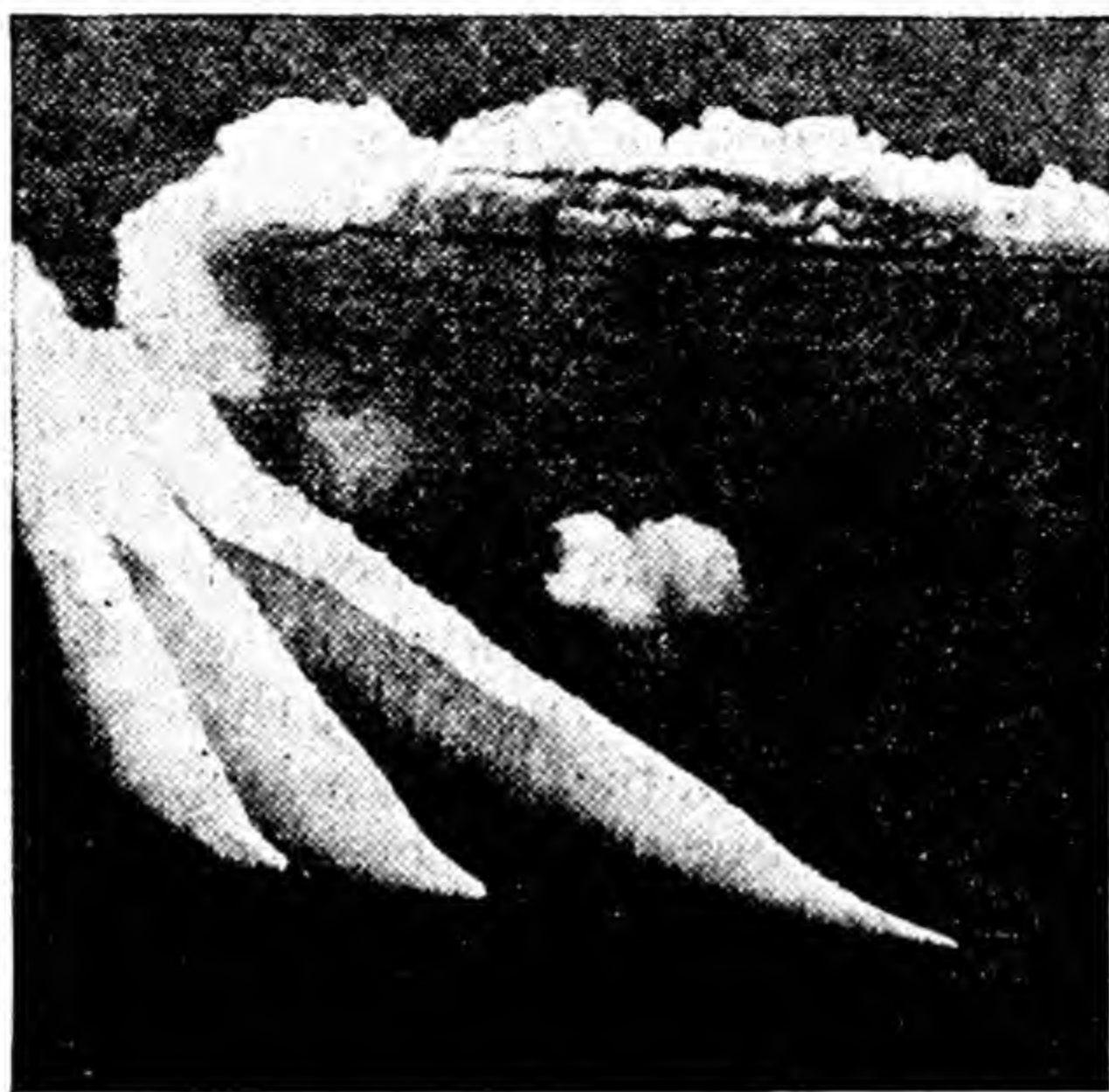
IMPORTANT ALLOYS OF TIN

<i>Alloy</i>	<i>Average Composition (Per Cent by Weight)</i>
Bronze.....	tin 15; copper 80; zinc 5
Solder.....	tin 50; lead 50
Babbitt.....	tin 90; lead 7; copper 3
Bell metal.....	tin 22; copper 78
Rose metal.....	tin 23; bismuth 50; lead 27
Pewter.....	tin 75; lead 25

A large amount of tin is used in the form of tinfoil wrappings. Most of the tubes containing toothpastes, shaving creams, and pharmaceutical preparations are made of tin.

Compounds. Tin forms two series of compounds. In stannous compounds the valence of tin is 2. In stannic compounds tin has a valence of 4.

Stannous chloride, a colorless crystalline solid, is made by dissolving tin in hydrochloric acid. In aqueous solution, the salt



Courtesy, U. S. Navy

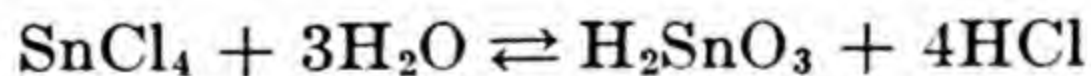
Fig. 167. A smoke screen. Stannous chloride and steam produce clouds of this type.

hydrolyzes extensively and the solution acquires an acid reaction and becomes cloudy because of the precipitation of a basic chloride:



To prevent this reaction, hydrochloric acid is added to stannous chloride solutions. The reversible reaction indicated in the last equation is then driven from right to left.

Stannic chloride, SnCl_4 , is a colorless liquid. It fumes in moist air, being hydrolyzed to hydrogen chloride and stannic acid:



The chlorides of tin, mixed with water vapor, form very efficient fogs which have been used as smoke screens.

The formula for stannic acid, H_2SnO_3 , implies that the compound is the monohydrate of stannic oxide; that is, it corresponds to the formula $\text{SnO}_2 \cdot \text{H}_2\text{O}$. As ordinarily prepared, the compound contains the oxide SnO_2 associated with an indefinite amount of water, and it is better, therefore, to refer to it as a *hydrous oxide of tin* and to write its formula as $\text{SnO}_2 \cdot n\text{H}_2\text{O}$. Stannic chloride is made by passing chlorine gas over hot tin.

Stannous sulfide is a brown insoluble compound, and *stannic sulfide* is yellow and also insoluble. The latter is used in gilding and bronzing.

Hydroxides. Tin forms two hydroxides: stannous hydroxide, $\text{Sn}(\text{OH})_2$; and stannic hydroxide, $\text{Sn}(\text{OH})_4$. They are more accurately represented as hydrous oxides, $\text{SnO} \cdot n\text{H}_2\text{O}$ and $\text{SnO}_2 \cdot n\text{H}_2\text{O}$. Both are amphoteric. When they neutralize bases, they form stannites and stannates, respectively.

Questions and Exercises

1. Write the formula for the principal minerals containing tin.
2. How is tin obtained from the ore?
3. What is tin plate and how is it made?
4. Name four alloys of tin.
5. What is the valence of tin (a) in stannous chloride, and (b) in stannic chloride?
6. Why is zinc not used in place of tin in the manufacture of cans used as containers for fruits and vegetables?
7. Account for the fact that tin was in use long before methods were developed for obtaining iron from its ores.
8. Would tin dissolve in a solution of copper sulfate? Would copper dissolve in a solution of stannous sulfate?
9. Calculate the weight of tin required to make 75 g. of stannous sulfate.
10. How would you make (a) stannic sulfide from stannic chloride, (b) stannous chloride from tin, (c) tin from stannic oxide?
11. Which dissolves faster in dilute acid, tin or iron? Explain how tin on tin plates and zinc on galvanized wire act to protect iron from corrosion.
12. Write an equation for the neutralization of $\text{Sn}(\text{OH})_2$ with sodium hydroxide.
13. Write an equation representing the neutralization of $\text{Sn}(\text{OH})_4$ with sodium hydroxide.
14. Write equations representing the neutralization of $\text{Sn}(\text{OH})_2$ and of $\text{Sn}(\text{OH})_4$ with hydrochloric acid, and show, by equations, what water would do to the products formed by these neutralizations.

PART 2

Lead

Occurrence. The element lead was known to the early Egyptians and Babylonians. Articles made of lead probably as early as 3000 B.C. have been found. Before the dawn of the Christian era the Romans used lead pipe for carrying water.

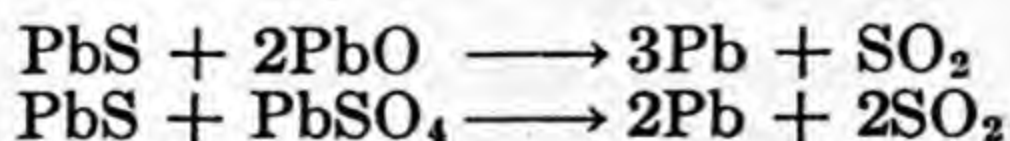
A few deposits of free lead exist, but the chief source of the world's supply of the metal is the sulfide, galena (PbS). The symbol, Pb, is derived from the Latin name *plumbum*.

Deposits of galena, a soft, gray, crystalline mineral, are found in nearly all countries. The United States leads in the production of lead. The most important mines of this metal are located in Missouri, Idaho, Utah, and Colorado, but there are smaller deposits in almost every state in the Union. The world production of lead amounts to approximately 2,000,000 tons annually, of which the United States produces about one-third.

Extraction. Most of the lead ore runs about 5 to 10 per cent metal. The first step in its metallurgy is concentration, which is successfully carried out by the flotation process (see page 376). The ore is then roasted—that is, heated in contact with air—in a reverberatory furnace until part of it has been converted into lead oxide, PbO , and lead sulfate, PbSO_4 :



The supply of air is then shut off and the heating is continued. Lead is liberated from the hot mixture through the following reactions:



The molten lead is drawn off and allowed to cool in molds.

Lead ore often contains silver. The separation of lead and silver is accomplished by Parke's process, which was described under the metallurgy of silver.

The Betts process. The electrolytic refining of lead is similar to the process used in refining copper. The electrodes are made

of pure lead. Pure lead plates out on one electrode, while the other metals, present as impurities, fall to the bottom of the cell or become dissolved in the electrolyte.

Properties and uses. Lead is the heaviest of the common metals. It is soft and malleable but has very little tensile strength. When heated, lead may be forced by hydraulic pressure through dies to form seamless lead pipe or rolled into thin sheets (foil). A freshly cut surface of lead has a silvery luster, but it tarnishes rapidly owing to the formation of a thin film of lead oxide which, in turn, reacts with moisture and carbon dioxide of the air, forming a basic carbonate of lead. This layer protects the metal from further action of water or air. Although most natural waters would soon line lead pipes with an impervious layer of insoluble salts, we do not ordinarily take the risk of using lead pipes to supply water for household use, since all lead salts are poisonous. Lead salts are easily taken into the blood stream, but they are excreted with difficulty. When taken continually, even in very small amounts, lead accumulates in the system until a poisonous dose is attained. Painters who work with lead pigments often become afflicted with lead poisoning, a condition sometimes known as "painter's colic."

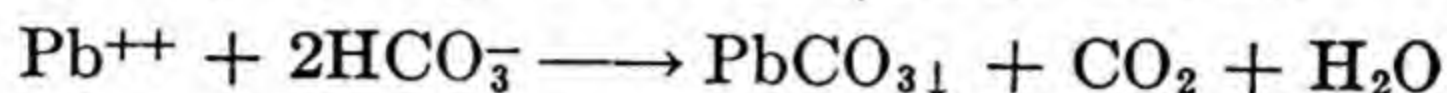
Nitric acid dissolves lead readily, forming lead nitrate and liberating oxides of nitrogen. Hydrochloric acid acts upon the metal very slowly, forming lead chloride, a compound which is soluble in hot water but relatively insoluble in cold water. Sulphuric acid fails to dissolve lead at an appreciable rate. The insoluble lead sulfate formed when the acid is first applied coats the metal and prevents further action. This property makes lead valuable for lining the chambers used in the manufacture of sulfuric acid, for covering laboratory desks, for drainpipes, and for lining sinks.

Lead is hardened by dissolving in the molten metal a little antimony. Type metal and shot contain small amounts of antimony. Common alloys of lead were mentioned in connection with tin. Lead is used principally in the manufacture of white lead, storage batteries, and cable coverings, and in plumbing.

Oxides. Ordinary lead oxide, or *litharge*, PbO , varies in color from light buff to yellow. It is the principal product formed when lead is heated in contact with air. It is used to a large extent in the manufacture of lead glass, in the rubber industry, and in the preparation of boiled linseed oil, for use in the manufacture of paints. *Lead dioxide*, PbO_2 , is a reddish-brown powder. It is used as an oxidizing agent in many industrial processes. The positive plates in storage batteries are made of lead dioxide.

Red lead, Pb_3O_4 , is made by heating litharge at temperatures between 450° and 550°C . in an atmosphere of oxygen. It is used as a pigment in the manufacture of red paint, glass, and glazes. Red lead may be considered a compound of litharge, PbO , and lead dioxide, PbO_2 . From this viewpoint its formula would be written $2\text{PbO} \cdot \text{PbO}_2$.

Lead carbonate. Sodium bicarbonate acts upon a solution of lead nitrate, precipitating lead carbonate, PbCO_3 :



Normal sodium carbonate precipitates the lead in the form of a basic carbonate, $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$. This may be regarded as a double compound of lead carbonate and lead hydroxide, and the formula may be written $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$. The basic carbonate is commonly called *white lead*. A solution of normal sodium carbonate has an alkaline reaction due to hydrolysis. It contains a greater concentration of OH^- ions than does a solution of sodium bicarbonate. This hydroxide-ion concentration accounts for the formation of the basic carbonate of lead by the action of normal sodium carbonate solution.

White lead. In the United States alone more than 150,000 tons of lead are used annually for the production of the basic lead carbonate, which is used in the manufacture of paints. White paint is made by incorporating a finely ground white opaque powder in linseed oil. Several white bodies are suitable for this purpose. Among the best are white lead, zinc oxide, titanium oxide, and barium sulfate. Nearly 75,000 tons of titanium oxide, TiO_2 , are used annually in the manufacture of paint. White lead is gradually darkened by traces of hydrogen sulfide in the air, the darkening being due to the formation of the black lead sulfide; but in spite of this disadvantage it continues to be the favorite white pigment.

On exposure to the air, linseed oil oxidizes and hardens to a tough elastic film which adheres to the surface it covers. At the same time, it holds firmly the opaque powder (body) and the pigments which impart the desired colors. Colored paints are made by adding colored metallic oxides or salts (or, in some cases, organic dyes) to the suspension of white lead in linseed oil. Lead chromate, PbCrO_4 , is a beautiful yellow solid known as *chrome yellow*. It is practically insoluble in water and is used as a pigment. Red lead, Pb_3O_4 , and Venetian red, Fe_2O_3 , are other pigments in common use.

White lead is made by the Carter process, which subjects finely powdered lead to the action of acetic acid and carbon

dioxide. Lead is powdered or atomized by directing a jet of superheated steam against a thin stream of the melted metal. The atomized metal is then placed in a wooden cylinder about 6 feet in diameter and 10 feet long, and the cylinder is slowly revolved. Carbon dioxide is forced into the cylinder through the center of the head, and at intervals the metal is sprayed with dilute acetic acid (vinegar). Acetic acid and oxygen convert the lead into basic lead acetate, $\text{Pb}(\text{OH})(\text{C}_2\text{H}_3\text{O}_2)$, and this compound is changed by water and carbon dioxide into the insoluble basic carbonate $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$. The time required is about 15 days. No heat is required beyond that produced in the chemical reactions that occur within the cylinder.

The Dutch process, which has been in commercial operation for 300 years, involves the same reactions, but the technique is different. Vinegar is placed in clay pots, and porous layers of sheet lead, called buckles, are placed above the vinegar in the pots. The pots are then covered with spent tanbark (originally barnyard manure was used). The fermentation of the tanbark or manure develops heat enough to vaporize the acetic acid. The vapor corrodes the lead, forming lead acetate, and through the fermentation and decay of the tanbark the necessary carbon dioxide is produced. The time required for the completion of the operation is between 100 and 130 days. The white lead is then separated from the unaltered lead and ground in water, strained through fine sieves, and then dried and ground with oil.

Lead acetate. "Sugar of lead," as lead acetate is often called, is prepared by dissolving litharge in acetic acid. A solution of lead acetate has a sweet taste and is very poisonous. It is used in dyeing and printing cloth and in the manufacture of hair dyes.

Lead sulfide. Lead sulfide is a black solid that appears as a precipitate when hydrogen sulfide is added to a solution containing lead ions. It is one of the most insoluble of the sulfides.

Lead sulfate. Lead sulfate is formed when a soluble sulfate is added to the solution of a lead salt. It is sometimes used as a white pigment.

Tetraethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4$. This is a liquid organic compound which, even in minute quantities, suppresses the knock in internal-combustion engines. Gasoline containing a small quantity of tetraethyl lead is sold as "ethyl gasoline."

Questions and Exercises

1. What is the composition of the commonest ore of lead? What is the name of this ore?
2. Briefly describe the smelting of lead sulfide ore.

3. Explain Parke's process for separating silver and lead.
4. Describe a method for making white lead.
5. Write an equation representing the action of nitric acid on lead. (Review the action of nitric acid on copper, page 379.)
6. Describe the result of mixing a solution of potassium chromate, K_2CrO_4 , and a solution of lead nitrate, $Pb(NO_3)_2$.
7. Enumerate four uses of metallic lead.
8. What purpose does white lead serve in colored paints?
9. Why is paint containing white lead undesirable for interior painting in cities?
10. Make a guess at the derivation of the word "plumber." Check your guess by consulting a dictionary.
11. What other elements besides tin and lead have you studied that belong to the fourth group of the periodic system?
12. How would you make (a) lead nitrate from lead, (b) lead chloride from lead nitrate, (c) lead sulfate from lead nitrate, (d) lead sulfate from lead chloride?

UNIT XVII

Subgroup VI of the Periodic Table: Chromium, Molybdenum, Tungsten, and Uranium

PART 1

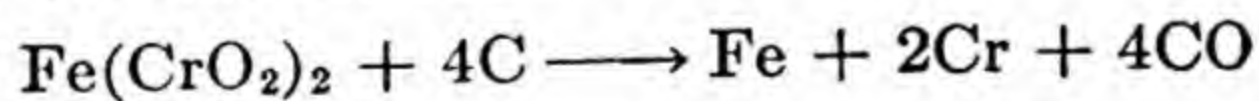
Chromium

We have studied in detail the properties of oxygen and sulfur, the first two members of Group VI. Chromium, molybdenum, tungsten, and uranium form a subgroup closely related to the main group elements. These metals form both acids and bases, uranium being the most strongly basic. The most basic element, as we have seen, is generally located at the bottom of the group.

Occurrence. The ores of chromium have been known for more than a century and a half, but the free metal has only recently become of commercial importance. The name *chromium* comes from the Greek meaning "color" because of the variety of colors found in its compounds.

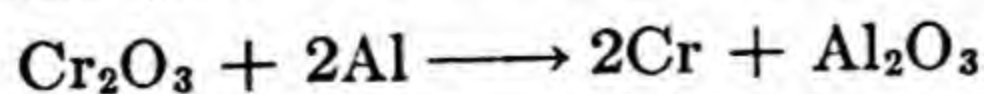
Preparation of the free metal. The commercial source of chromium is a mineral called *chromite*. It is an oxide of iron and chromium corresponding to the formula $\text{Fe}(\text{CrO}_2)_2$ or $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. The countries which have most of the known deposits of chromite are Russia, Africa, Turkey, India, and Greece. The United States produces a substantial quantity of chromite ore, but most of the chromium used in this country is imported.

Extraction. Chromium is liberated from the ore by reduction with carbon in an electric furnace:



The chromium obtained from chromite in this way contains iron and carbon.

Chromium free from carbon is obtained by reducing chromic oxide with aluminum (the Goldschmidt process):



The powdered ore is mixed with aluminum, and heat is applied to the mixture at one point to start the reaction. Then the heat

generated by the chemical change is sufficient to continue the process and to melt the chromium.

The electrolytic process for refining chromium has become very important in recent years. It produces a pure product which is malleable, while that obtained by reduction with carbon is quite brittle.

Properties. Chromium is a white metal closely resembling iron. It melts at 1615°C . and has a specific gravity somewhat less than that of iron. It can be polished, and the polished surface remains bright for a long time. Chromium containing carbon is brittle and is about as hard as glass.

Powdered chromium, when heated to a high temperature in air, burns readily. The metal dissolves in hydrochloric acid and in dilute sulfuric acid:



or



The chromous salt is not the final product, for these salts are oxidized by hydrogen ions to the chromic state:



Pure water furnishes hydrogen ions enough for this reaction. A chromous salt, therefore, has a short life in aqueous solution.

Uses. The chief use of chromium is in the manufacture of steel. Steel containing chromium is very hard. It is used in the manufacture of cutting tools, automobile gears and bearings, safes, vaults, armor plate, and rock-crushing machinery. Stainless steel is composed of iron, nickel, and chromium. Chromium is used in the manufacture of electric heaters. Alloys of nickel and chromium, called *nichrome* and *chromel*, are used as resistance coils. These alloys have a high electrical resistance, and they are not rapidly oxidized by the air even when red-hot. Chromium-plated parts are used extensively in the automobile industry. Radiators are now electrically plated with chromium. The metal is so hard that it cannot be polished by the methods applied to other metals, but it retains its high luster for a long period of time. Bathroom and kitchen fixtures also are plated with chromium.

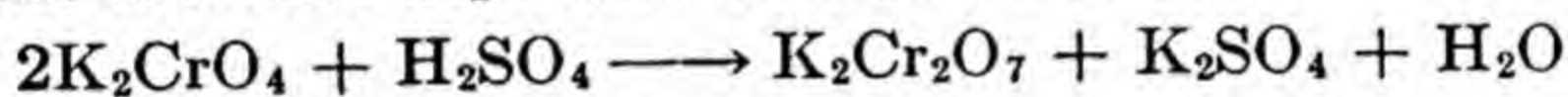
Compounds. Chromium forms compounds in which it has a valence of 2, 3, or 6. Chromous chloride, CrCl_2 , is colorless in the solid state. It has a blue color when dissolved in water, but the color changes to green in a short time because of oxidation of the chromous to chromic ions. Hydrogen gas escapes slowly from the solution as the oxidation of the chromous salt proceeds. Solid chromic chloride, CrCl_3 , has a reddish-violet color. It dissolves very slowly in water, forming a green solution.

Chromic sulfate is made by dissolving chromic hydroxide, $\text{Cr}(\text{OH})_3$, in sulfuric acid. It forms reddish-violet crystals containing 15 moles of water: $\text{Cr}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$. It dissolves in water, forming a bluish-violet solution which, like other solutions of chromic salts, becomes green when heated to the boiling point. It is thought that the violet solution contains the ions $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ (six water molecules associated with each Cr^{+++} ion).

In addition to chromous and chromic salts in which chromium appears as the positive ion, compounds exist in which this element is a constituent of negative ions. The chromates are salts of chromic acid, H_2CrO_4 , and the dichromates are salts of dichromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$. These acids are unstable compounds, but their salts are stable and easily prepared.

Chromates. Potassium chromate is a pale yellow, soluble salt. Its formula is K_2CrO_4 or $\text{K}_2\text{O} \cdot \text{CrO}_3$. In solution it ionizes to form CrO_4^{--} ions and K^+ ions. A solution of potassium chromate when added to a solution containing a lead or barium salt precipitates the insoluble lead chromate PbCrO_4 , or barium chromate, BaCrO_4 .

Dichromates. Concentrated sulfuric acid converts a chromate into a dichromate. Potassium dichromate, a red crystalline salt, has the formula $\text{K}_2\text{Cr}_2\text{O}_7$ or $\text{K}_2\text{O} \cdot 2\text{CrO}_3$.



The conversion of a dichromate into a chromate, the reverse of the above reaction, is accomplished by treating the former with a base.



Questions and Exercises

1. Describe chromium and mention two uses for the metal.
2. How is metallic chromium obtained from chromic oxide?
3. What is the ratio between the weight of iron and the weight of chromium formed when chromite is heated with coke in an electric furnace?
4. Write an equation representing the burning of chromium in air.
5. Potassium dichromate and ferrous sulfate in acid solution react as follows:

$$\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{FeSO}_4 + 7\text{H}_2\text{SO}_4 \rightarrow 3\text{Fe}_2(\text{SO}_4)_3 + \text{Cr}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 7\text{H}_2\text{O}$$
 Write the equation in an ionic form, omitting the ions that take no part in the reaction.
6. Write the formulas for (a) sodium chromate, (b) sodium dichromate, (c) chromic sulfate.
7. Name one household use for chromium.
8. Name some uses for alloys of chromium.
9. Why is chromium plating superior to other kinds of plating for automobile radiators and household fixtures?
10. What is stainless steel?

PART 2

Molybdenum, Tungsten, and Uranium

Molybdenum

Occurrence. Molybdenum occurs chiefly as lead molybdate, PbMoO_4 , and as molybdenum sulfide, MoS_2 . The latter is often found in flakes which resemble graphite and, like graphite, leave a mark on paper. Extensive deposits of molybdenum are found in Colorado, California, Canada, and Queensland.

Extraction. The ore is first roasted, then extracted with sodium hydroxide or ammonium hydroxide. Molybdates are obtained by this treatment: sodium molybdate, Na_2MoO_4 , or ammonium molybdate, $(\text{NH}_4)_2\text{MoO}_4$. On treatment with nitric acid, molybdic acid, H_2MoO_4 , is formed. The acid is changed to the oxide by heating, and the oxide is then reduced to the free element by heating it with hydrogen. Molybdenum may also be obtained either by reducing the oxide with zinc or with aluminum.

Properties. Molybdenum is a metal a little darker in color than platinum. When pure it is strong and malleable. The metal oxidizes very slowly in air at ordinary temperatures, but it burns readily when heated.

Uses. Molybdenum is added to steel to produce toughness, malleability, and ductility without loss of hardness. Its most important alloy is ferromolybdenum, which is used in the manufacture of molybdenum steel. Spades, shovels, and a variety of other common tools are made of this kind of steel. Molybdenum is used also in electric lamps to support the tungsten filaments. It is used for the terminals in spark plugs, and for coils in electric resistance furnaces.

Tungsten

Tungsten is a heavy metal (specific gravity 19.3). The name *tungsten* is derived from two Swedish words meaning "heavy stone." The German name for the metal is wolfram, and we use the symbol W for this element. Tungsten is found in many minerals, the common ones being scheelite, CaWO_4 , and ferberite,

FeWO_4 . Sodium tungstate, Na_2WO_4 , a soluble salt, is formed when any other tungstate is fused with sodium carbonate. To obtain the free metal from the fused mass, the soluble sodium tungstate is dissolved out of the mixture and the solution is then acidified with hydrochloric acid. Tungstic acid, H_2WO_4 , precipitates as a yellow powder:



Heat decomposes tungstic acid, leaving a residue of the yellow trioxide, WO_3 , and the free element is obtained by reducing the hot oxide with hydrogen:



Properties and uses. Tungsten is one of the heaviest and hardest metals known. It has an extremely high melting point ($3540^\circ\text{C}.$), higher than that of any other metal and exceeded only by that of carbon. This property makes it useful for electric light filaments, since the filament can be raised to a temperature at which an intense white light results without melting the metal.

Tungsten is used in place of platinum in electric contact points, for spark gaps in induction coils, for wiring electric furnaces, and as targets in X-ray tubes. It has great tensile strength and, when added to steel, imparts this property to the steel. Cutting tools made of tungsten steel are used in high-speed lathes; they retain their temper (hardness) even at red heat. *Carboloy*, a carbide of tungsten imbedded in cobalt, is an exceedingly hard product which is now used extensively for tools to be used in high-speed machines. A successful method for plating tungsten on copper, iron, and other metals has been devised. The tungsten plate adheres firmly to the metal on which it is deposited. It takes a high polish, resembling nickel or chromium plate, and it does not tarnish or corrode under ordinary conditions.

Uranium

Uranium is the heaviest known atom. It occurs in pitchblende and carnotite, ores which are valuable for their radium content. Mme. Curie obtained the first sample of radium from pitchblende produced in Bohemia. The richest deposits of uranium ore are found in the Belgian Congo. The deposits of pitchblende at Great Bear Lake near the Arctic Circle in Canada are yielding uranium and silver to a value of over \$1,125,000 annually.

The free metal is obtained from its oxides— U_3O_8 , which is called green oxide; and UO_2 , which is sold as black oxide—by reduction with carbon, aluminum, or calcium.

Questions and Exercises

1. How is molybdenum obtained from its ores?
2. Why is molybdenum added to steel?
3. From a consideration of its compounds does molybdenum have both metallic and nonmetallic properties?
4. Write the equation for the reduction of molybdenum oxide by the thermite process.
5. How is tungsten obtained from sodium tungstate, Na_2WO_4 ?
6. Give two uses for tungsten.
7. What is the chemical name for (a) scheelite, CaWO_4 , and (b) ferberite, FeWO_4 ?
8. Uranium is found in what ores?
9. Account for the fact that radium is a product obtained from uranium ores.
10. Is uranium a radioactive element?

UNIT XVIII

Subgroup VII of the Periodic Table:

Manganese and Rhenium

PART 1

Manganese

Manganese was for many years the only metal known in Subgroup VII of the periodic system. Rhenium was discovered in 1925. Manganese differs greatly from the elements in the main family of Group VII, but in its highest valence state its compounds closely resemble those of chlorine.

PHYSICAL PROPERTIES OF MANGANESE AND RHENIUM

	Mn	Re
Atomic number.....	25	75
Atomic weight.....	54.93	186.31
Isotopes.....	55	185,187
Melting point, °C.....	1220	3440
Boiling point, °C.....	2150	—
Density, grams per cubic centimeter.....	7.2	21.4

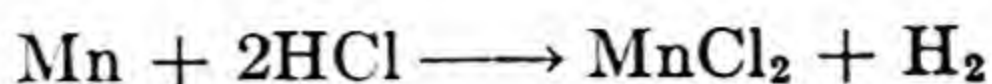
Occurrence. The principal ore of manganese is the oxide, MnO_2 , called *pyrolusite*. It is a black mineral which usually leaves a black stain when touched.

The annual world production of manganese is well over 5,000,000 tons. The main sources are Russia, British India, Gold Coast, Brazil, and Egypt. The United States is a small producer of manganese, but it consumes about one-fifth of the world's supply.

Extraction. Impure manganese is obtained by the reduction of the dioxide with carbon. Pure manganese is prepared by reduction of the oxide with aluminum.

Properties. Manganese has a steel-gray color faintly tinged with red. It is softer than iron when pure, but the impure metal, obtained by reduction with carbon, is brittle and harder than iron. The pure metal oxidizes readily in air and reacts slowly with water

at room temperature. Manganese dissolves in acids, liberating hydrogen:



or



Uses. Manganese is used principally in the manufacture of hard, tough steel. Plowshares, steel rails, and heavy machinery such as rock crushers are made of manganese steel. A bronze composed of copper, tin, zinc, and manganese is hard, strong, and resistant to the action of sea water. It is used in propeller blades for steamships. Manganin is a brass containing manganese. It is used in electrical resistance boxes. Spiegeleisen and other ferromanganese alloys are used extensively in the steel industry.

Compounds. In its lower valence states manganese forms salts in which manganese atoms constitute the positive ions. Manganous chloride, MnCl_2 , and manganous sulfate, MnSO_4 , are examples. There are many compounds in which manganese has a valence of 6 or 7. In all these compounds the manganese atom is found in the negative ion. *Potassium manganate* has the formula K_2MnO_4 . It is a dark-green crystalline solid. A solution of the compound is green. *Potassium permanganate*, KMnO_4 , is a purple crystalline salt. It is an excellent oxidizing agent and is commonly used for this purpose.

Oxides. Manganese forms the following compounds with oxygen: manganous oxide, MnO ; manganic oxide, Mn_2O_3 ; manganese dioxide, MnO_2 ; manganese trioxide, MnO_3 ; and manganese heptoxide, Mn_2O_7 . Of these oxides, manganese dioxide is the most important. We used it as a catalyst in the preparation of oxygen and as an oxidizing agent in the preparation of chlorine from hydrochloric acid.

This oxide is used also to remove the green color from glass containing iron compounds. Large quantities of it are consumed in the making of dry cells, and it finds employment as a drier in varnish and printing ink. About 25,000 tons of MnO_2 are used annually.

Questions and Exercises

1. How is manganese obtained from manganese dioxide?
2. State two uses for manganese.
3. Calculate the weight of aluminum that must be used to liberate 1 ton of manganese from its oxide.
4. Name some useful alloys of manganese.
5. Give several uses for manganese dioxide.
6. Write the equation for the oxidation of hydrochloric acid with manganese dioxide.

UNIT XIX

Iron, Cobalt, Nickel, and the Platinum Family

PART 1

Iron

Iron, cobalt, and nickel occupy a position following manganese in the Periodic Table. They have eight, nine, and ten valence electrons, respectively, and it would be logical to classify them as members of Groups VIII, IX, and X in the periodic system. The three elements are similar in properties, and in their most important compounds each has the valence number of +2 or +3. On account of these resemblances we place the three elements together as a "triad" under the headings A, B and C. (See page 119.) Iron, cobalt, and nickel are all magnetic and they form similar compounds. Two other triads, or groups of three similar elements, also are included in the A B C columns. They are rare elements, and since they are also useful, they constitute our most costly metals. Platinum is the best known of these rare elements.

The similarity between some of the physical properties of iron, cobalt, and nickel is shown in the table following:

SOME PHYSICAL PROPERTIES OF IRON, COBALT, AND NICKEL

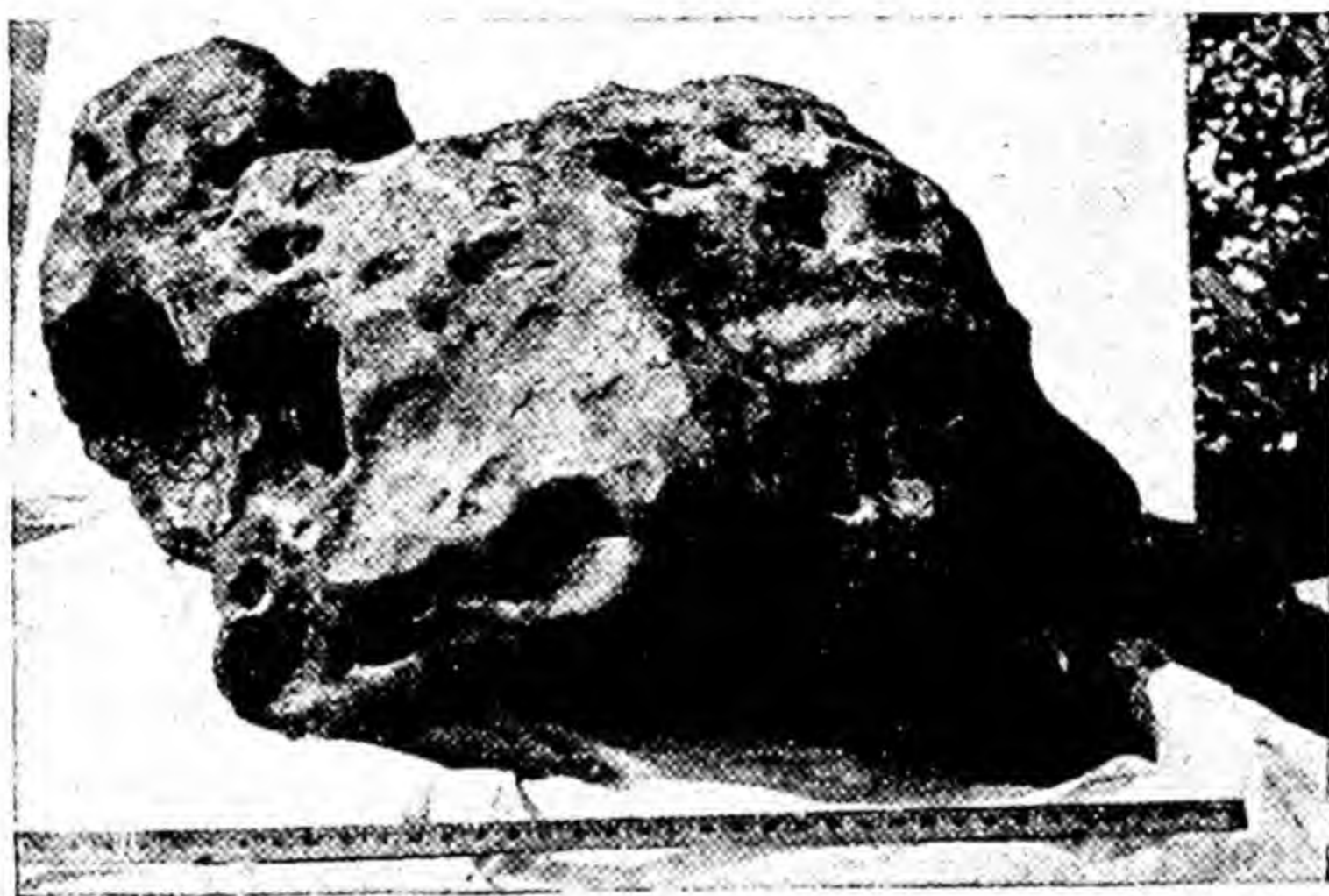
	Atomic number	Atomic weight	Density	Melting point	Principal valences
Iron.....	26	55.84	7.86	1530°C.	2 and 3
Cobalt.....	27	58.94	8.9	1490°C.	2 and 3
Nickel.....	28	58.69	8.9	1452°C.	2

Iron is the most important metal on the earth. Its ores are widely distributed and easily reduced. The metal has properties which make it extremely useful. These properties can be changed to suit our needs by the addition of small amounts of other elements.

Occurrence. The percentage of iron in the crust of the earth is comparatively small. At greater depths, however, the amount

of iron is thought to increase rapidly, and the interior of the earth may consist largely of iron. We know that our earth is a large magnet; therefore it must be composed largely of magnetic substances. Meteors which have fallen on the earth are masses of iron, usually containing some nickel and cobalt. There is no reason to assume that our planet differs greatly in composition from the others in the universe. If this reasoning is true, iron is the most abundant metal everywhere.

There are several ores of iron. Hematite, Fe_2O_3 , has a red color. It is largely responsible for the red color in the soil of



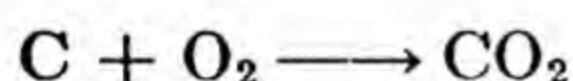
Courtesy, Earle G. Linsley, Chabot Observatory

Fig. 168. The Goose Lake Meteor. This meteor, found in Modoc County, California, in 1938, weighs 2573 pounds. It is now the property of the Smithsonian Institution in Washington.

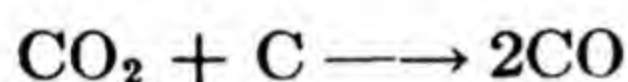
parts of our country and in rocks. *Magnetite*, which is a black ore found extensively in Sweden, has the formula Fe_3O_4 or $\text{FeO} \cdot \text{Fe}_2\text{O}_3$. Some of the deposits of this ore are magnetic, and are called *lodestone*. *Limonite* is brown in color, and is represented by the formula $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The common sulfide, iron pyrite, FeS_2 , is found in yellow flakes or crystals which are often mistaken for gold, and the compound is known as "fool's gold." The carbonate, FeCO_3 , is also found extensively in our own country. The world's annual production of iron is about 172 million metric tons, and nearly all this supply is derived from iron oxides and carbonates. The United States produces more than 70,000,000 tons of iron annually.

The manufacture of iron. Impure iron is obtained by the reduction of an iron ore with coke. The smelting of the iron ore to make cast iron, commonly called *pig iron*, is accomplished in a blast furnace. The operation of the blast furnace may be

followed by referring to Fig. 169. Iron ore, limestone, and coke in proper proportions are dumped into the hopper at the top. When the hopper is full, the bell-shaped top, *D*, is lowered and the charge falls into the furnace. The purpose of the bell is to distribute the charge and to seal the top of the furnace. At the bottom, air is forced into the furnace through ducts, *A*, in the sides. These ducts are known as tuyères. The oxygen of the air combines with the coke to form carbon dioxide:



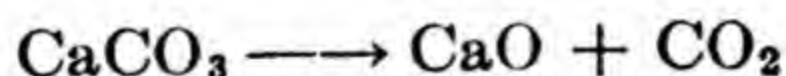
As the hot carbon dioxide passes upward, it comes in contact with more coke and is reduced to carbon monoxide:



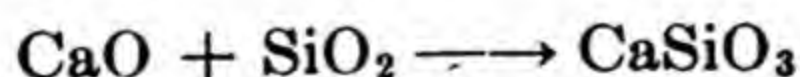
The iron ore descending from the top of the furnace comes in contact with the rising carbon monoxide gas, and in the region of the furnace where the temperature is about 500°C . iron oxide is reduced to iron according to the reaction:



The limestone is added to combine with silica, which is in the ore. If the ore were pure Fe_2O_3 and the coke pure carbon, no limestone would be necessary. By the heat of the furnace the limestone is converted to calcium oxide:



The calcium oxide combines with silica, to form calcium silicate:



When the charge reaches a lower section of the furnace, where the temperature is very high, both the silicate (known as slag) and the iron melt and run to the bottom. The slag, being lighter than molten iron, floats on the liquefied metal and is drawn off

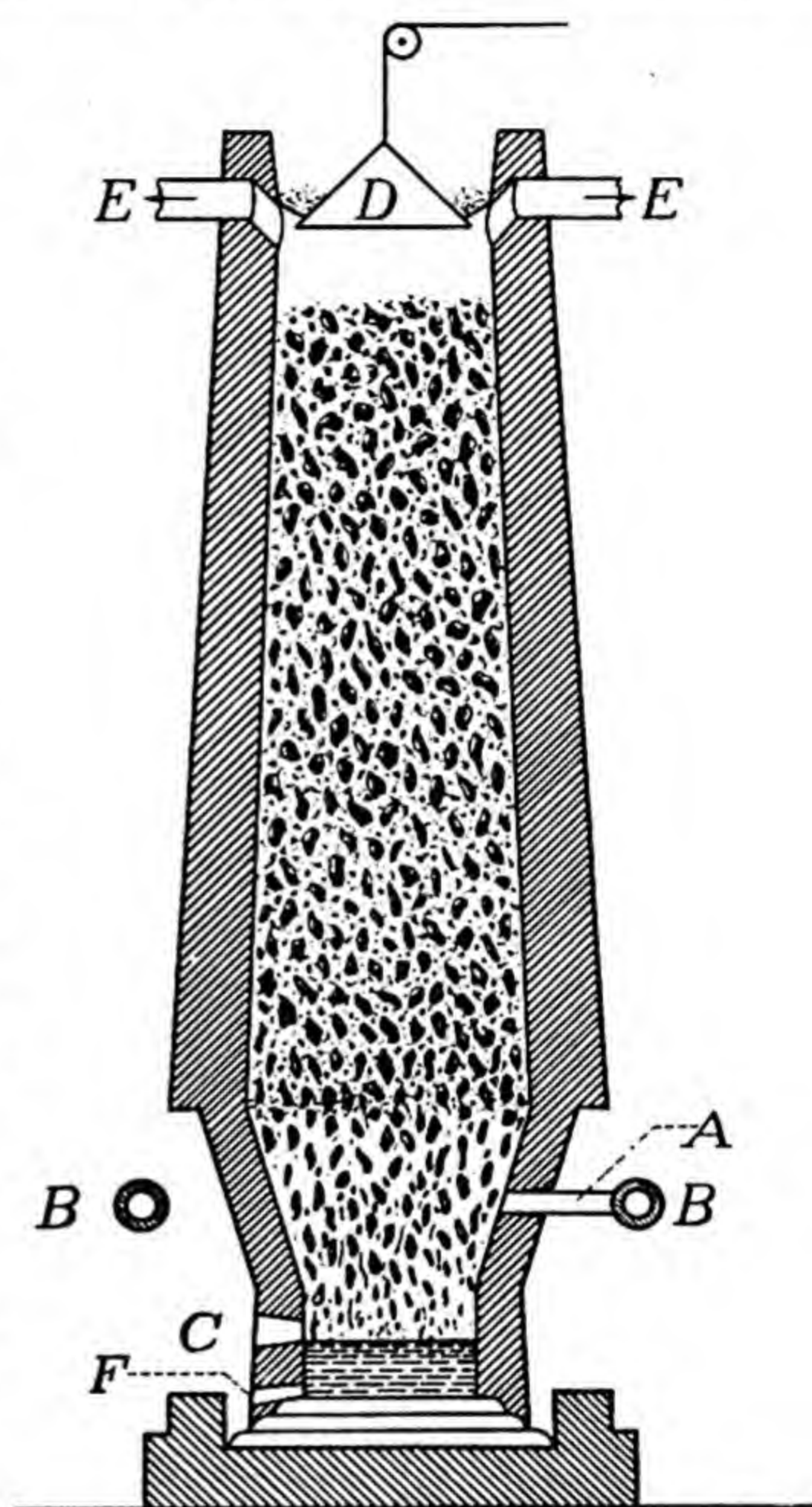


Fig. 169. Diagram of the blast furnace.

at *C*. The iron is drawn off at *F*. The slag was once dumped as a waste product, but today it is utilized in the manufacture of cement.

The largest furnaces are about as high as a 10-story building and are capable of producing 800 to 1000 tons of pig iron in one day. The blast furnace is one of the largest of all chemical-reaction chambers.

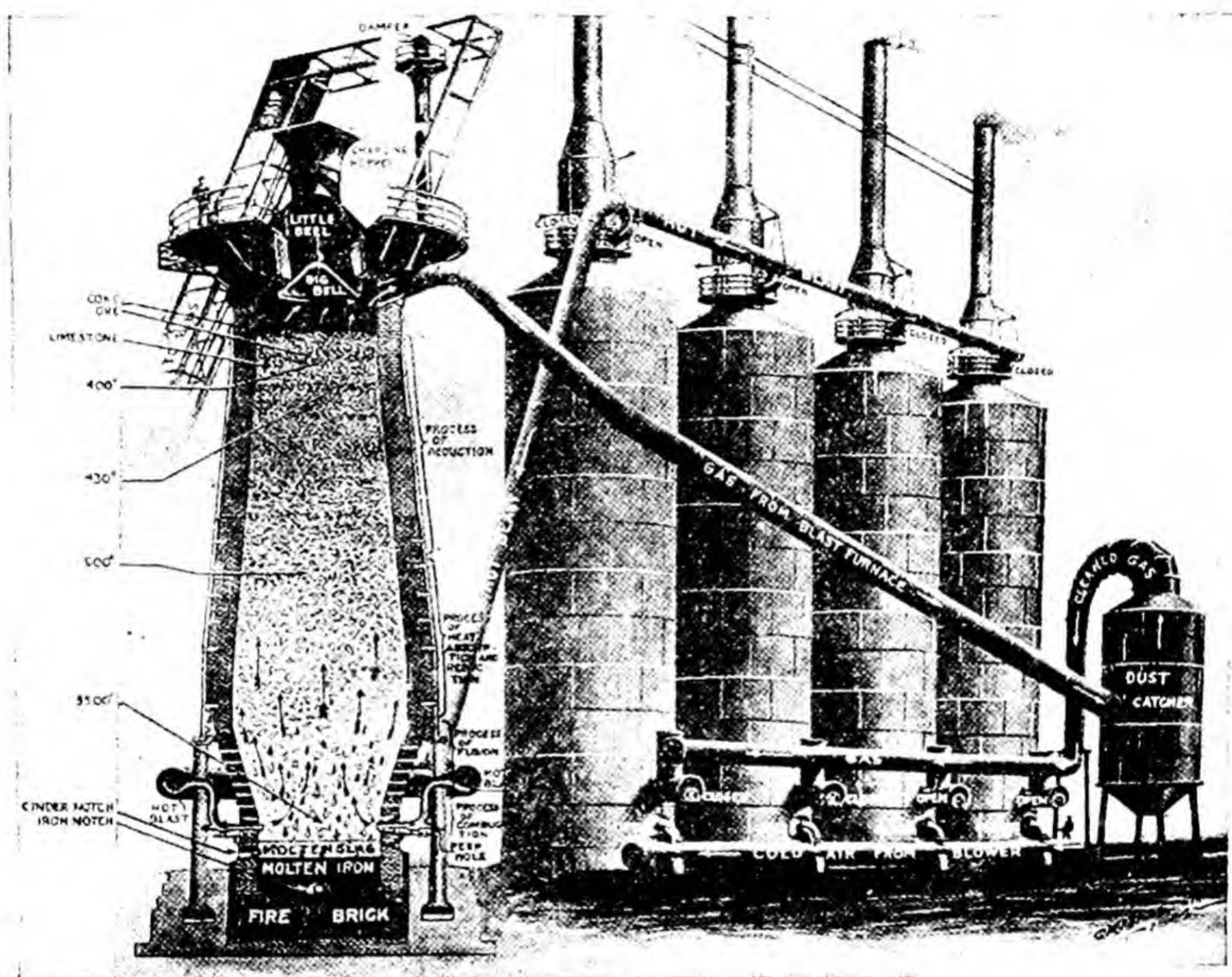
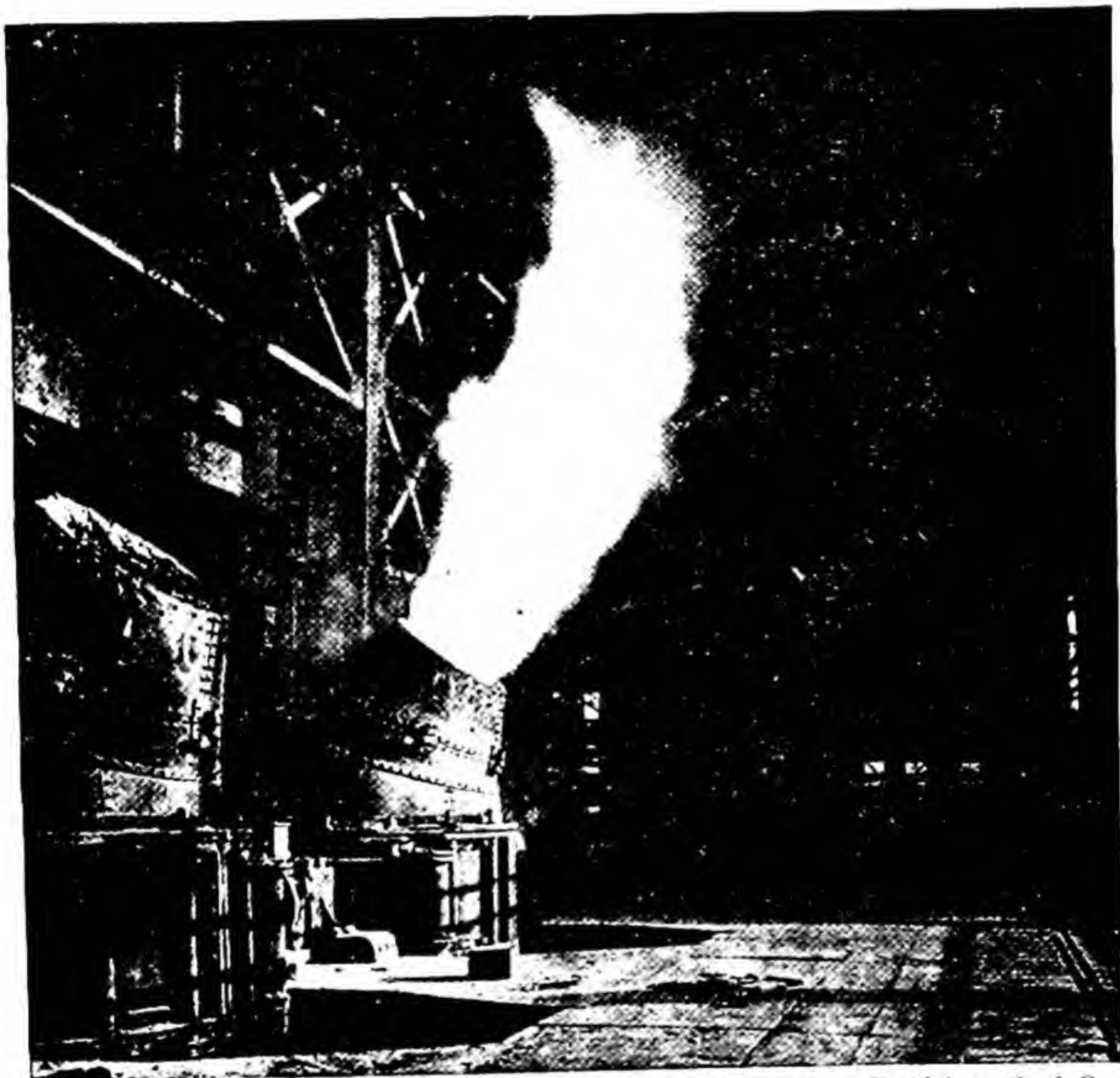


Fig. 170. Blast furnace and stoves.

Properties and uses of cast iron. Pig iron, or cast iron, contains carbon derived from the coke; and silicon, manganese, sulfur, and phosphorus, derived principally from the ore. When the liquid is cooled rapidly, the carbon remains in combination with the iron; the product, called white cast iron, is then brittle. But when the liquid is cooled slowly, much of the carbon separates as graphite, and the product, called gray cast iron, is softer and tougher. Sulfur causes the metal to become brittle when hot (causes "red-shortness"), and phosphorus produces a metal which is very brittle at ordinary temperatures ("cold-shortness"). Cast iron is not malleable and cannot be welded. It is used in making objects which are not to be subjected to sudden shocks.

Stoves, radiators, machine bases, and automobile engine blocks are made of cast iron.

Steel. Ordinary steel is iron containing less carbon, sulfur, and phosphorus than are present in cast iron. Steel contains from $\frac{1}{10}$ per cent to $1\frac{1}{2}$ per cent carbon, and cast iron may contain as much as 4 per cent carbon. The process of making steel from cast iron consists in the removal of most of the carbon and as much as possible of the sulfur and phosphorus. Steel is made by several processes, as indicated below.



Courtesy, Bethlehem Steel Co.

Fig. 171. A Bessemer converter.

The Bessemer process. A Bessemer converter is shown in Fig. 171. About 15 tons of molten cast iron are poured into this pear-shaped container, and air is blown through the mass. The air combines with the carbon and silicon, producing sufficient heat to keep the iron liquefied. The carbon and silicon are burned out of the charge in about 10 minutes. A large flame fills the mouth of the converter, and the operator can judge by the color of the flame when the process is completed. A calculated amount of iron containing a relatively large amount of carbon and manganese is then added to give the steel the desired carbon and man-

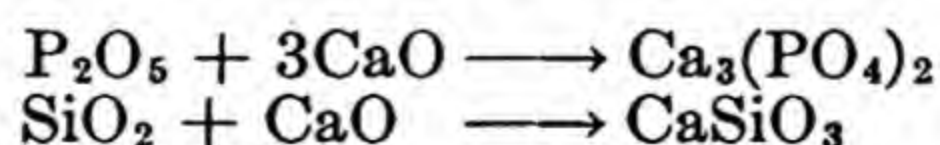
ganese content, and a final blast of air is used to mix the molten mass thoroughly. The converter is tipped on the trunnions, and the contents are poured into a ladle, and from the ladle the molten mass is cast in molds. The variation in the composition of the contents with the time of the blow is given below.

ANALYSIS OF A TYPICAL BESSEMER BLOW
(Parts per 100 parts of iron)

Minutes after beginning the blow	C	Si	Mn	P	S
0	4.00	1.00	.50	.080	.070
2	3.90	.70	.20	.081	.071
4	3.50	.35	.07	.082	.071
6	1.80	.03	.03	.083	.072
8	.90	.02	.02	.084	.073
10	.05	.01	.01	.085	.074

While the carbon, silicon, and manganese are almost completely burned out of the iron, the phosphorus and sulfur are not removed by this method. The steel made in this way is of low grade and is used principally in the manufacture of wire, nails, pipes, and reinforcing rods for concrete.

The open-hearth process. In the open-hearth furnace the molten iron to be purified is placed in a large shallow oven and is kept hot by the burning of gas over its surface. The foreign substances are oxidized by the excess oxygen in the flame. The gas and air which enter the open-hearth furnace are preheated in passing over a hot checkerwork of bricks. The outgoing gas passes through a similar chamber and thus heats bricks on the opposite side of the hearth. About every 20 minutes the direction of the flow of the air and gas is reversed, and in this way the heat of the exhaust gas is utilized. The furnace is usually lined with limestone, which, at the temperature employed, is converted into calcium oxide, and the latter combines with the oxidized phosphorus and silicon, removing them from the molten metal:



The carbon dioxide formed at the same time passes off as a gas, and the sulfur is removed largely in the form of calcium sulfide, CaS , in the slag. The process usually takes about eight hours. An analysis of the melt is made from time to time, and the process can be stopped when the steel contains the desired

amount of carbon. The contents of the furnace are then drained off and cast into ingots (large blocks), which are rolled, while hot, into the desired shapes. In this country more than 90 per cent of the ordinary steel is made by this method.

The electric-furnace method. The finer grades of steel are made in electric furnaces. A basic slag is added to the iron to remove sulfur and phosphorus, and the whole mass is melted by electric arcs between the electrodes.

Dissolved gases and dissolved oxides of iron, which are detrimental to good steel, are reduced to a minimum by this process since the steel does not come in contact with a flame. The composition of electric-process steel can be very accurately controlled. In some electric furnaces 50 or 60 tons of steel can be purified in each run, but most of the furnaces have smaller capacities. Electric-process steel is used mainly at the present time for fine tools.

Wrought iron. Wrought iron differs from steel in that the carbon as well as the phosphorus, sulfur, and silicon are removed or reduced to a minimum. Wrought iron is the purest iron that is made on a large scale. It contains no iron carbide, but, owing to the porous character of the metal, it does contain small particles of slag. Wrought iron is produced by heating cast iron in a reverberatory furnace with ferric oxide and limestone. The mixture is heated in much the same way as in the open-hearth furnace. In the reverberatory furnace, however, the flame does not come directly in contact with the molten mass. The ceiling of the reverberatory furnace is heated by the flame, and the iron is melted by radiation from the hot ceiling. The foreign elements in the iron, including carbon, are oxidized chiefly by iron oxide, Fe_2O_3 , which is used to line the furnace.

The liquefied mass is stirred or "puddled" to insure contact with the lining of the furnace. The carbon monoxide, formed by the oxidation of the carbon in the iron, burns on the surface of the metal, while the oxides of silicon, sulfur, and phosphorus form a slag with the lime. As the impurities are removed, the melting point of the iron increases. Cast iron melts at about $1200^\circ\text{C}.$; pure iron melts at $1530^\circ\text{C}.$ When the iron is nearly pure, it begins to solidify and becomes pasty. It is then gathered into balls or "blooms" and withdrawn from the furnace. The hot iron is hammered to remove adhering slag, then rolled or pressed into the desired forms.

Properties and uses of wrought iron. Wrought iron is soft, ductile, and malleable and can be easily welded. It is much more resistant to corrosion than the ordinary steels, and for this reason

it is used in the manufacture of galvanized sheet iron which is to be exposed to weathering.

The process of making pure iron is simplified in Sweden, for the magnetite ore, Fe_3O_4 , is almost free from undesirable impurities. Charcoal instead of coke is used in the smelting. Charcoal contains practically no sulfur or phosphorus.

Crucible steel. Molten wrought iron slowly dissolves carbon. This principle is employed in the manufacture of crucible steel or electric-furnace steel. Wrought iron, or very low-carbon steel, is melted in large graphite crucibles while in contact with charcoal. The iron is kept molten long enough to permit it to acquire the desired carbon content. Steel made in this way is very hard, but not too brittle for use in the manufacture of tools. Axes, dies, and cutlery are made of crucible steel of low carbon content. Files, drills, razor blades, and watch springs are manufactured from crucible steel of high carbon content.

Alloy steels. The addition to steel of relatively small amounts of different metals causes remarkable changes in the properties of the metal.

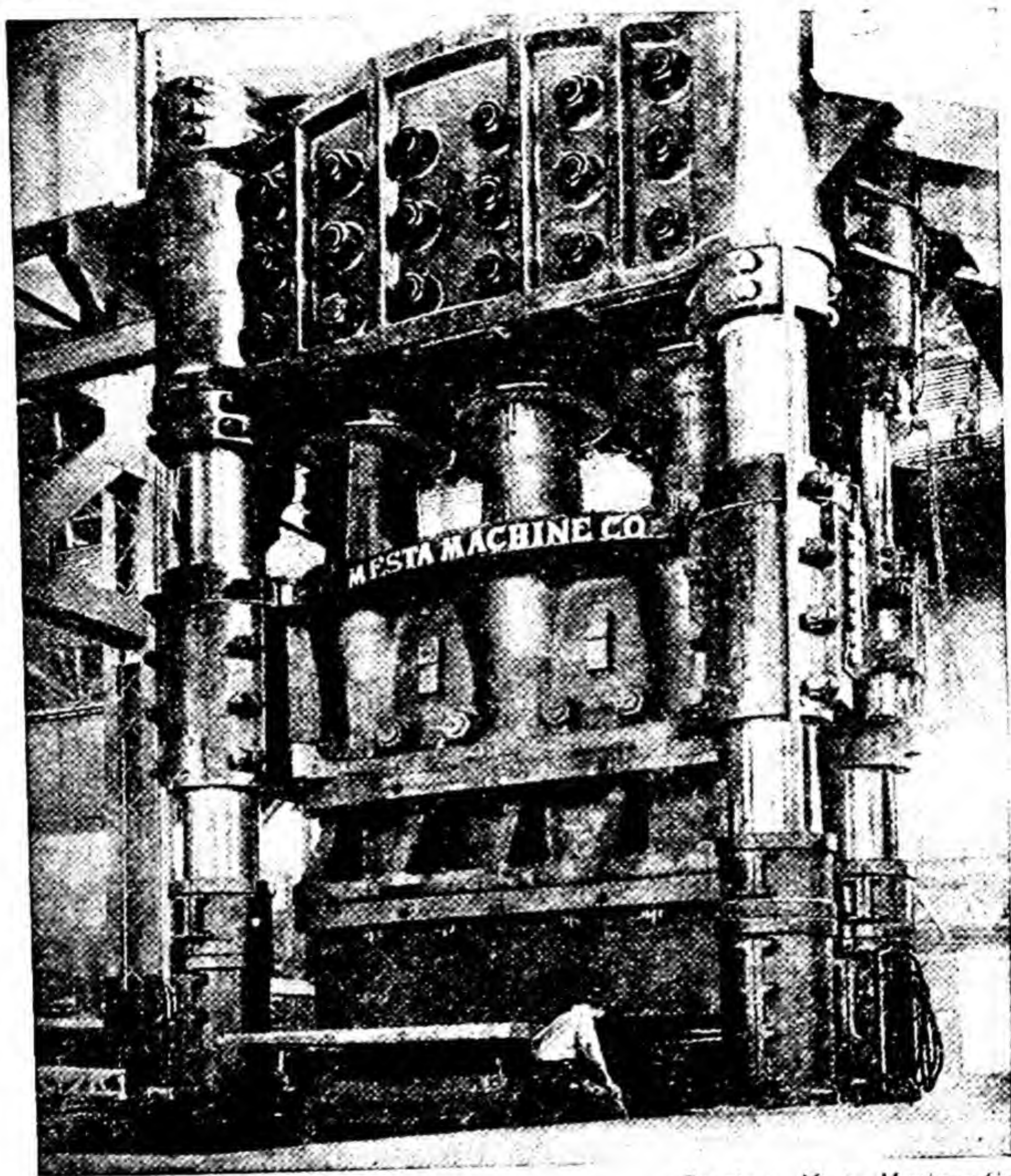
Nickel steel. Steel containing a small amount of nickel has more than double the strength of ordinary steel without being less ductile. Steel containing 35 per cent nickel is known as *invar*. Invar does not expand or contract appreciably when the temperature changes, and it is therefore useful for measuring instruments, surveyors' tapes, and pendulums. Steel with 46 per cent nickel expands with the temperature to the same extent that certain kinds of glass expand. It is therefore useful in making wire seals in glass such as are used in electric light bulbs.

Stainless steel, an alloy of chromium and iron, contains from about 9 to 25 per cent chromium. *Allegheny metal* contains about 18 per cent chromium and 8 per cent nickel, the remainder iron. These alloys are very resistant to corrosion, but the addition of small percentages of other elements are sometimes necessary to maintain corrosion resistance under certain service conditions or after heating within a certain temperature range.

Tungsten steel has the property of retaining its "temper" even when red-hot. At red heat ordinary steel tools become soft and useless. Lathes and other machines with cutting parts made of ordinary steel must be run slowly enough to prevent these tools from becoming very hot. When tungsten steel tools are used, the machines may be run at high speeds. This discovery has doubled the rate of production in many factories.

Cobalt steel is used in the manufacture of razor blades and permanent magnets. *Manganese steel* is employed in the manu-

facture of rock crushers, plowshares, safes, and railroad rails, especially for rails to be used on curves, where the wear is great. Chromium imparts hardness, and when chromium and manganese are both added to steel, the product is hard and tough and particularly suited to the manufacture of armor plate and automobile crankshafts.



Courtesy, Mesta Machine Co.

Fig. 172. Heavy machinery is used in cutting and shaping steel.

Tempering the steel. Molten iron dissolves carbon, forming a carbide of iron called cementite, Fe_3C , which is soluble in iron. When the molten steel solidifies quickly, it still holds the cementite in the form of a solid solution; that is, in the form of separate molecules of cementite uniformly distributed among the iron molecules. As the solid steel is cooled, the cementite has a tendency to form small clusters or aggregates of cementite molecules instead of remaining uniformly distributed in the iron. When the steel is cooled very slowly, this separation actually

occurs, and with the aid of a microscope the aggregates can be seen. The small grains of cementite are themselves hard, but most of the steel in which these grains are embedded contains little or no carbon and is, therefore, soft. A very soft steel is produced in this way.

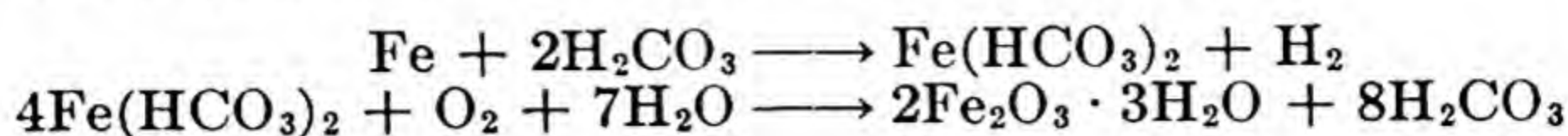
If the hot steel is cooled quickly by quenching in water, the cementite does not have time to precipitate and it remains in solution (uniformly distributed) in the solid iron. Such a steel is very hard. The process of separating the cementite from the iron can be controlled, and as much hardness as is desirable can be retained. This process of adjusting the hardness of steel is called *tempering*. Tempering or heat treatment is carried out as follows: Hot steel is quenched in water or oil, leaving the cementite in the dissolved state; that is, uniformly dispersed throughout the mass. The steel is then heated to a dull red heat and kept at this temperature long enough to permit the desired amount of separation or crystallization of the cementite. It is then quenched again to stop the process. The blacksmith tempers the edge of a tool by heating the entire tool to redness, then dipping the edge to be tempered into water. The whole piece is not quenched, and a part of the tool remains hot. Heat flows from the hot portion to the tip, and as the temperature of the edge is again raised, the separation of the hard and soft components of the steel occurs. When the desired amount of tempering is attained, the whole piece is cooled by dipping it in water, and the process is stopped. As the heat flows out to the edge of the tool, colors appear on the surface of the tempered metal. These colors are due to very thin layers of oxide on the surface. Each color indicates a certain hardness, and the tempering is controlled by watching the development of color. The colors that appear in various stages of the tempering process are light yellow, a straw color, brown, purple, and blue.

Pure iron. Pure iron can be prepared by the reduction of iron compounds with hydrogen. If hydrogen is passed over pure ferric oxide at a high temperature, the Fe_2O_3 is reduced to iron:



Pure iron has a white, lustrous appearance. It is ductile and malleable and does not rust as rapidly as does an impure form of the metal. When iron rusts, it first reacts with carbonic acid, forming ferrous bicarbonate, which in turn is oxidized by the air to ferric oxide. Carbonic acid (carbon dioxide and water) dissolves iron, slowly forming ferrous bicarbonate, $\text{Fe}(\text{HCO}_3)_2$, and

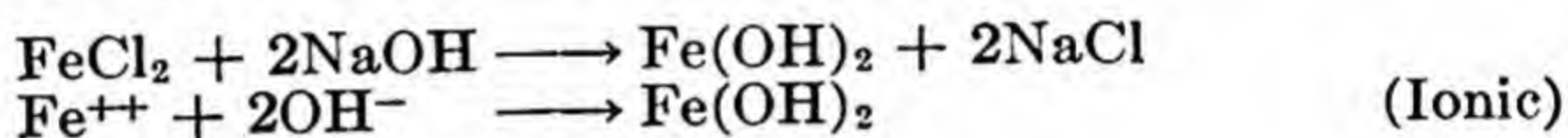
hydrogen gas. The $\text{Fe}(\text{HCO}_3)_2$ is then oxidized to $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, which is rust, and carbonic acid is regenerated:



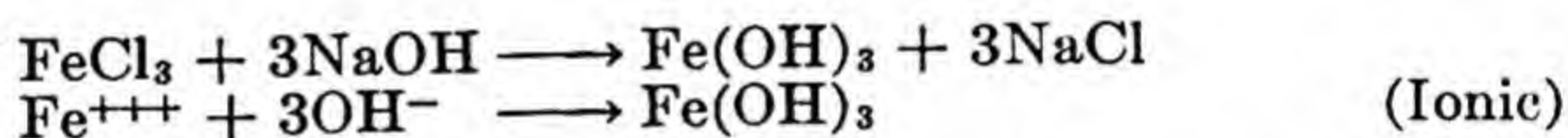
Since iron reacts with carbonic acid, liberating hydrogen, we might predict that iron will dissolve in any acid which, in solution, gives an appreciable concentration of hydrogen ions. Iron dissolves rapidly in dilute hydrochloric acid or sulfuric acid, liberating hydrogen. Cold concentrated sulfuric acid, on the other hand, acts so slowly upon iron that the acid can be shipped in iron drums or in iron tank cars.

Iron forms two classes of compounds: *ferrous* compounds in which the valence of the iron is 2, and *ferric* compounds in which its valence is 3.

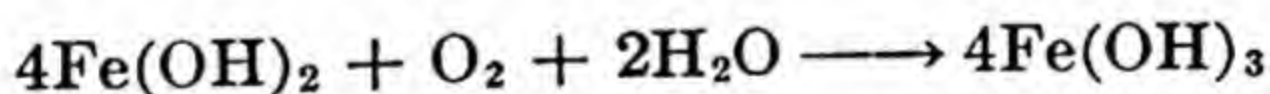
The hydroxides and oxides of iron. Ferrous hydroxide can be made by the addition of a base, such as sodium or ammonium hydroxide, to a solution of a ferrous salt. Ferric hydroxide can be made by adding a base to a solution of a ferric salt:



or

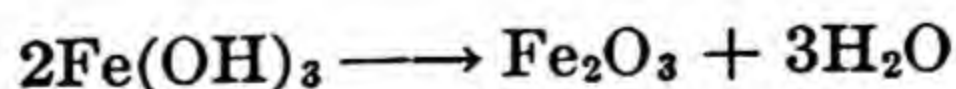


These hydroxides are relatively insoluble. Ferrous hydroxide is light green in color, while ferric hydroxide is reddish-brown. The green ferrous hydroxide when exposed to air and water turns brown, owing to the formation of ferric hydroxide according to the reaction



Although we write the formula $\text{Fe}(\text{OH})_3$ for ferric hydroxide, the compound as ordinarily prepared is hydrous ferric oxide, $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$; that is, it is ferric oxide combined with an indefinite quantity of water.

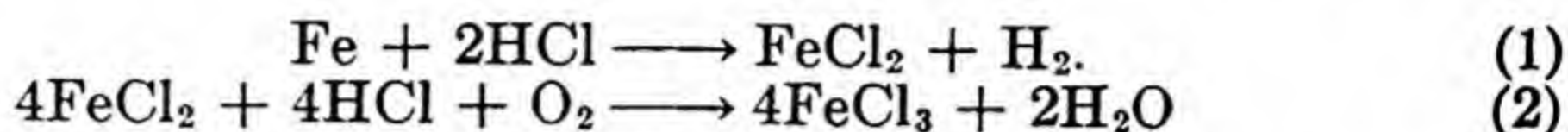
Ferric oxide can be made by heating ferric hydroxide to a high temperature:



The oxide made in this way is known as *rouge* or *Venetian red* and is used as a pigment. It is employed also as an abrasive in polishing glass. The ore hematite is an impure form of ferric oxide. Ferrous oxide, FeO , is unstable in air. It combines with oxygen to form ferric oxide.

The salts of iron. The commonest salts of iron are those derived from hydrochloric acid, sulfuric acid, and nitric acid. These salts are soluble in water. The ferrous salts are green and the ferric salts brown.

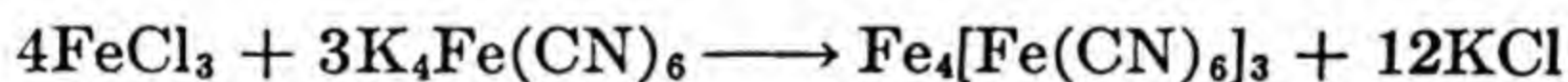
Ferrous chloride is formed when iron dissolves in hydrochloric acid in the absence of air. In the presence of air *ferric chloride* is formed:



Ferrous sulfate is made by the action of dilute sulfuric acid on iron. Waste liquors from the refining of petroleum contain sulfuric acid, and since it is not permissible to run an acid into sewers or streams, the sulfuric acid is converted into ferrous sulfate by treatment with scrap iron.

Ferrous sulfate, known also as *green vitriol* or *copperas*, is used in the manufacture of ink. When ferrous sulfate is mixed with a solution of tannic acid, some ferrous tannate is formed. This is an almost colorless substance, but on exposure to air it is oxidized to ferric tannate, which is black. Blue-black ink contains a blue dye to give the original blue color, and also ferrous tannate, which later forms the fast black ferric tannate. Ferrous sulfate is used also in the dyeing industry and as a deodorant, a disinfectant, and a wood preservative.

Tests for iron salts. The presence of the ferric ion may be determined by the use of potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$. When this is added to the solution, a deep blue precipitate of ferric ferrocyanide (*Prussian blue*) is obtained:



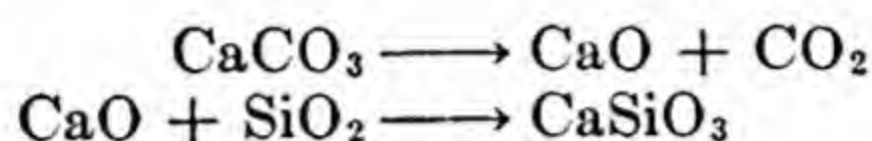
Similarly, a solution of potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, is used as a test for ferrous ions by the formation of a dark blue precipitate of ferrous ferricyanide, $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$. This is called *Turnbull's blue*.



Questions and Exercises

1. How is iron obtained from iron oxide?
2. Account for the fact that iron is seldom found in the free state.
3. Iron ore usually contains silica. How is this removed in the smelting process?
4. Name the elements that are present in cast iron.
5. How does cast iron differ from pure iron in physical properties?

6. How is steel made from cast iron?
7. How does cast iron differ from steel?
8. Name six elements that are used with iron to produce alloys having certain desired qualities.
9. How is steel tempered?
10. What is wrought iron?
11. What weight of limestone is needed to remove one ton of silica from an iron ore?



12. Can wrought iron be tempered? Explain.
13. What advantage does tungsten steel have over ordinary steel?
14. What is the valence of iron in ferrous carbonate? Is the conversion of ferrous carbonate into free iron a process of oxidation or reduction? The valence of any element in the free state is 0.
15. Whenever one substance is reduced, some other substance must be oxidized. Name the substance that is oxidized and the substance that is reduced when ferric oxide is heated with coke and limestone.
16. Explain how two different samples of steel having the same composition may have very different properties.
17. For what kind of products is Bessemer steel used? Could open-hearth steel be used equally well in each case?
18. A sample of steel weighing 1 g. was burned by passing air or oxygen over it in a hot tube. The carbon dioxide formed in the process was absorbed by soda lime (a mixture of NaOH and CaO) and the gain in weight of the soda lime due to the absorption of carbon dioxide was 0.0185 g. What weight of carbon was necessary to produce this amount of carbon dioxide? What was the percentage of carbon in the original sample of steel?
19. What is the composition of iron rust?
20. What compound is formed when carbon dioxide and water act upon iron?
21. What is formed when carbon dioxide, water, and oxygen act upon iron?
22. What is the valence of iron (a) in ferrous compounds and (b) in ferric compounds?
23. Why do some blue inks turn black on exposure to air?
24. What is (a) green vitriol, (b) blue vitriol, (c) rouge?

PART 2

Cobalt and Nickel

Cobalt

Occurrence. Cobalt was first prepared from its ore in 1735. Before that time metallurgists had been puzzled by an ore that looked like copper ore but from which they could obtain no copper. They called the ore *kobold* from the German word meaning *goblin*, because they thought the ore was possessed by evil spirits. When the metal was finally isolated, it was called cobalt.

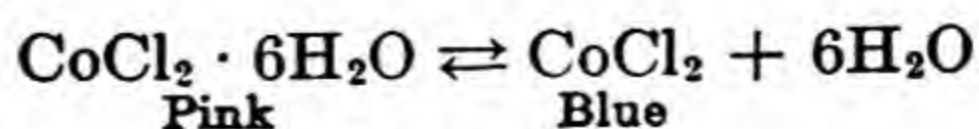
The principal ores of cobalt are smaltite, CoAs_2 , and cobaltite, CoAsS . They are obtained principally from Canada, the Belgian Congo, and South Rhodesia.

Extraction. The ore is changed to the oxide when heated in the presence of air, and the metal is obtained by reduction of the oxide with carbon or with hydrogen.

Properties and uses. Cobalt is a white metal, with a faint pink tinge. The chemical properties of cobalt are similar to those of iron except that it is less easily dissolved by acids and, in general, it is less reactive than iron. Like iron, it is attracted by a magnet. Pure cobalt is used in the preparation of grinding tools made of carboloy, which is an alloy of iron, tungsten, and cobalt. Cobalt is a component of the steels used for razor blades, surgical instruments, and electromagnets. Metallic cobalt and its compounds are used also as catalysts in certain organic reactions. The oxide, when mixed with other metallic oxides, is used as an absorbent in gas masks.

Compounds. Cobalt compounds have few commercial uses. Cobaltous oxide, CoO , is used to impart a deep blue color to glass. It is used also for blue coloring in decorating porcelain ware.

Cobaltous chloride exists in two colors, blue and pink. When CoCl_2 crystallizes from water, it forms a hydrated salt, which is pink, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and when this salt is heated or exposed to dry air the water evaporates, leaving anhydrous cobalt chloride, CoCl_2 , which is blue:



When a solution of cobalt chloride is used as ink, often called "sympathetic ink," the writing is not discernible until it is heated. It then turns blue and can be read. When the writing is moistened in a jet of steam, the reaction shown above proceeds from right to left and the writing again becomes pale pink in color and almost invisible. The same reaction is used in a simple device for indicating the humidity of the air. A surface covered with cobaltous chloride, such as strips of cloth or the dress of a doll, is pink when the air is saturated with water vapor and blue when the humidity is low. Cobaltous nitrate and sulfate are both soluble salts. When alkali is added to the solution, the pink hydroxide $\text{Co}(\text{OH})_2$ is formed.

The simple salts of trivalent cobalt, such as CoCl_3 and $\text{Co}(\text{NO}_3)_3$, are unstable, but complex compounds of trivalent cobalt, such as $\text{K}_3\text{Co}(\text{NO}_2)_6$, are easily prepared. In potassium cobaltinitrite and in other stable cobaltic compounds the cobalt atom is contained in the negative ion.

Nickel

Occurrence. Nickel is found in combination with sulfur and with arsenic in Ontario, Canada; in New Caledonia, an island lying east of Australia; in British India; and in Norway and Finland. It is also one of the usual components of meteors.

Properties and uses. Nickel is a hard, white metal which is malleable and magnetic. It can be polished readily and maintains a high luster in the air for a long period.

The chemical properties of nickel are very much like those of iron and cobalt, but it does not tarnish or react with acids as easily as do iron and cobalt. It dissolves in nitric acid and aqua regia. Alkalies affect it only slightly.

Finely divided nickel is used as a catalyst, especially in the hydrogenation of oils. It finds extensive use in plating other metals, but in this capacity it has a real rival in chromium. Nickel is used extensively in the preparation of special alloys (see Nickel steel, page 446). In addition to nickel steels, important alloys of nickel are German silver (Ni, Cu, and Zn), monel metal (Ni, Fe, and Cu), nickel coin alloy (Ni and Cu), nichrome (Ni, Cr, and Fe). The latter is used for making electrical-resistance wire like that employed in the manufacture of electrical toasters.

Compounds. Nickel forms two oxides, NiO and Ni_2O_3 . The latter, however, is believed to be a mixture of NiO and NiO_2 . The corresponding hydroxides also exist. Nickelous salts are important, but nickelic salts are unknown.

The important soluble salts of nickel are the acetate, nitrate, sulfate, chloride, and the double salt, nickel ammonium chloride. The solutions of the salts are green in color. The anhydrous salts are yellow or brown.

Questions and Exercises

1. In what way does iron resemble cobalt and nickel?
2. State two uses for nickel and two uses for cobalt.
3. Name several alloys containing nickel.
4. Devise a method for distinguishing iron from nickel.
5. What weight of water would be released if 50 g. of crystallized cobalt chloride were heated?
6. Name some objects that are commonly plated with nickel.
7. How did cobalt receive its name?
8. What is "sympathetic ink"?

PART 3

The Platinum Metals

The other two triads, which with iron, cobalt, and nickel make up Group VIII of the Periodic Table, are called the *platinum metals*. These six metals are ruthenium, rhodium, palladium, and osmium, iridium, and platinum. They are all similar to platinum in properties. The table below summarizes some of the physical constants of these metals.

SOME PHYSICAL CONSTANTS OF GROUP VIII

	Atomic number	Atomic weight	Density	Melting point, °C.	Specific heat	Oxides
Ruthenium.....	44	101.7	12.20	2450	0.0611	RuO, Ru ₂ O ₃ RuO ₂ , RuO ₄
Rhodium.....	45	102.91	12.50	1995	0.058	RhO, Rh ₂ O ₃ RhO ₂
Palladium.....	46	106.7	12.10	1555	0.059	PdO, PdO ₂
Osmium.....	76	190.8	22.48	2700	0.0311	OsO, Os ₂ O ₃ OsO ₂ , Os ₃ O ₄
Iridium.....	77	193.1	22.40	2350	0.0323	Ir ₂ O ₃ , IrO ₂
Platinum.....	78	195.25	21.45	1770	0.0323	PtO, PtO ₂

Occurrence. The platinum metals are all found in the native state, usually associated together and mixed with gold, silver, copper, nickel, and iron. They occur in alluvial sands in the Ural Mountains in Russia and in Colombia, South Africa, the Congo, Borneo, and Canada. Small amounts are found in the United States. The annual production of platinum is approximately 500,000 troy ounces. Canada is the largest producer and Russia has second place. The United States contributes about 20,000 troy ounces yearly to the world's supply.

Platinum

Properties and uses. Platinum is a soft, white metal with a silvery luster. The name is derived from a Spanish word meaning

“little silver.” It is very malleable and ductile. The coefficient of expansion of this metal is so near that of glass that it is used for wires which must be sealed in glass, as in electric light bulbs and laboratory apparatus. Because of its high melting point and resistance to chemical corrosion, it is used extensively for laboratory equipment such as crucibles, wire, and sheet. It is, however, attacked by chlorine and aqua regia, as well as by fused alkalis.

Platinum occurs in several forms. *Spongy platinum* is a gray, porous mass which readily absorbs hydrogen and serves as a powerful catalyst in reactions involving the addition of hydrogen to other substances. *Platinum black* is a fine powder produced by the reduction of platinic chloride. It adsorbs both oxygen and hydrogen with great rapidity and causes a mixture of the two gases to explode. Gas lighters have been made on this principle. *Hard platinum* is an alloy of platinum, usually with other metals in this group. Platinum is used extensively in dentistry and in jewelry.

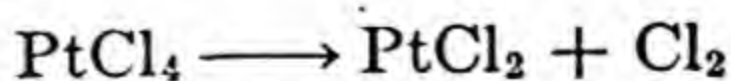
Compounds. Platinum forms two series of compounds, in which it has valences of 2 and 4.

Platinum chloride, PtCl_2 , is formed when chlorine is passed over finely divided platinum at 240° to 250°C . When platinum chloride is dissolved in hydrochloric acid, it forms chloroplatinous acid, H_2PtCl_4 . The potassium salt of this acid, K_2PtCl_4 , is used in photography.

Platinous hydroxide, $\text{Pt}(\text{OH})_2$, is formed by the addition of a base to a solution of platinous chloride. On heating, it yields metallic platinum.

Chloroplatinic acid, H_2PtCl_6 , is the product formed when platinum is dissolved in aqua regia. The solid crystalline compound, having the formula $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, is obtained on evaporation of the solution. A solution of this acid is used in the quantitative determination of potassium, since it forms insoluble potassium chloroplatinate, K_2PtCl_6 .

Platinic chloride, PtCl_4 , is formed when chloroplatinic acid is ignited in an atmosphere of chlorine. When this salt is heated to 370°C ., it decomposes according to the following equation:



PtCl_3 , the trichloride, possibly forms as an intermediate product.

Platinic hydroxide, $\text{Pt}(\text{OH})_4$, may be formed by the addition of sodium carbonate to a solution of chloroplatinic acid. When the solution is evaporated to dryness, the residue has the composition $\text{Pt}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ or $\text{H}_2\text{Pt}(\text{OH})_6$.

Palladium

Palladium is harder than platinum, and is less ductile and malleable. It has the lowest melting point of the platinum group. It is oxidized slightly when heated to a dull redness, forming a blue, superficial coating of the oxide, PdO . Palladium is acted upon readily by the halogens and, unlike platinum, is soluble in nitric acid. The most outstanding property of palladium is its ability to adsorb hydrogen. Colloidal palladium will adsorb almost 3000 times its volume of hydrogen, and palladium black will adsorb 1200 volumes of the gas. Hence palladium is a powerful catalyst for many gas reactions.

Since palladium is highly resistant to the action of oxygen, moisture, and hydrogen sulfide, it is often used for the mechanisms of watches, fine balance beams, surgical instruments, and other special apparatus. It is used also for contact points in telephone relays.

Palladium is mixed with gold to form alloys such as *palau*, *palorium*, and *rhotanium*, which have properties making them useful as substitutes for platinum in jewelry, dentistry, and laboratory apparatus.

Iridium

Iridium is a white metal with a bluish tint. It is not acted upon by oxygen at ordinary temperatures, but at 1100°C . it becomes covered with a purple layer of the oxide. The hot metal reacts with chlorine, but acids and aqua regia have very little effect upon it.

Iridium forms several alloys. Platinum is usually mixed with 2 per cent of iridium in order to harden it for commercial use. Alloys containing from 10 to 50 per cent of iridium are used for electrical equipment and chemical apparatus. The standard weights and standard units of length which are so closely guarded in a vault near Paris are made of a platinum alloy containing 10.1 per cent of iridium.

Many surgical instruments, hypodermic needles, bearings for watches and compasses, and fountain-pen points are made from iridium alloys. Because of its scarcity and usefulness, iridium is the most expensive of the platinum metals.

Questions and Exercises

1. Name the elements of the platinum group.
2. Mention some resemblances between members of each of the triads in this group.

3. What properties make platinum indispensable for scientific use?
4. Name several uses for each member of the platinum group.
5. Why are these metals usually found in the native state rather than in the form of compounds?
6. What is the heaviest known element?
7. Write the formula for a compound in which platinum has a valence of (a) 2, and (b) 4.

UNIT XX

Carbon Compounds

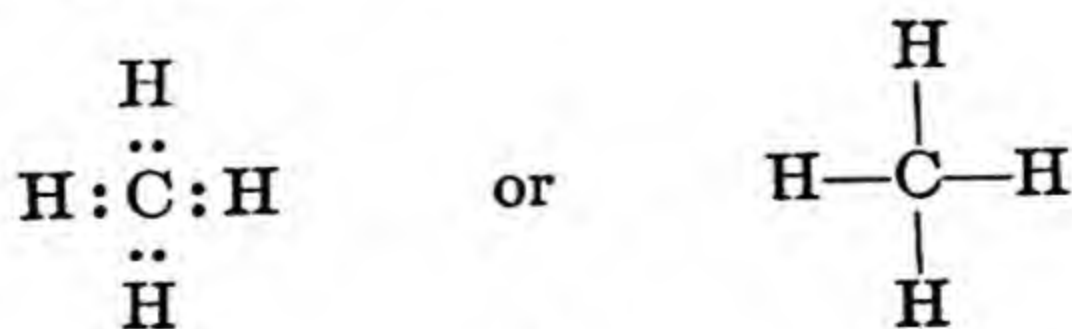
PART 1

The Hydrocarbons

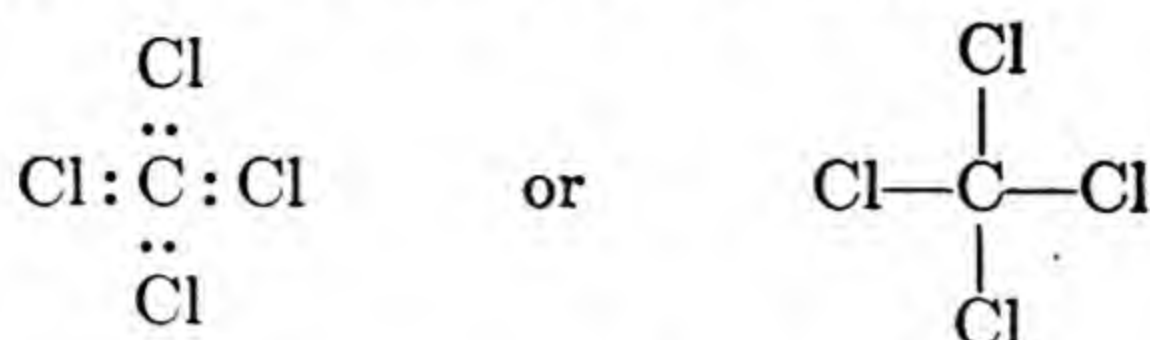
Carbon differs from other elements in its remarkable capacity to form complex compounds. Except in compounds of carbon we seldom find more than two or three atoms of the same kind attached to each other. In hydrogen peroxide, H—O—O—H , two oxygen atoms are present in a chainlike structure, and there are many organic compounds that contain chains of two or three nitrogen atoms. In some compounds of boron and of silicon there are chains of four or five atoms of the same kind, but longer chains than these are rare. On the other hand, compounds containing more than 60 carbon atoms in continuous chains are known.

Compounds of carbon are called *organic compounds*, for they were first obtained from living organisms—plants and animals. It was formerly supposed that the formation of these compounds was dependent upon processes occurring in the living cells of plants and animals. We now know that organic chemistry is governed by the same forces that apply to compounds of the mineral kingdom. Many of the compounds which exist in living tissues and which are products of life processes in the animal organism have been prepared artificially in the laboratory.

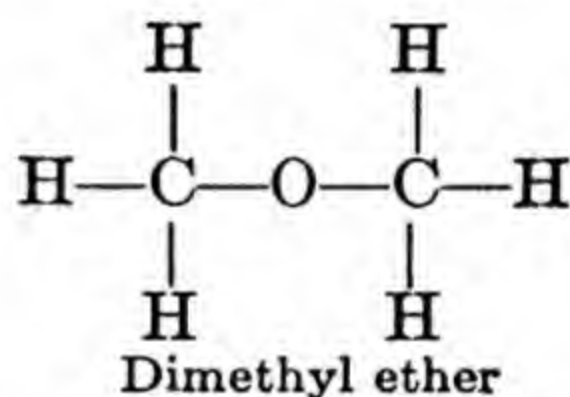
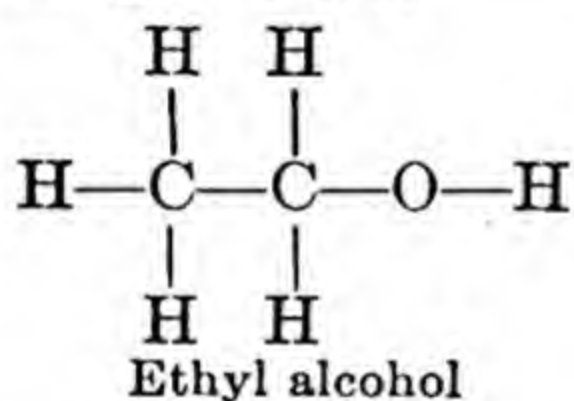
Structural formulas. Carbon has a valence of 4 in nearly all its compounds. It shares four pairs of electrons with hydrogen atoms in the compound known as methane, CH_4 , and it shares four pairs of electrons with chlorine atoms in carbon tetrachloride, CCl_4 , a liquid which is used as a fire extinguisher. The formula of methane may be written:



and the formula for carbon tetrachloride is:



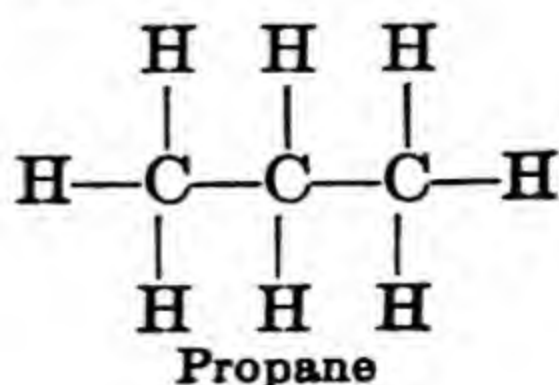
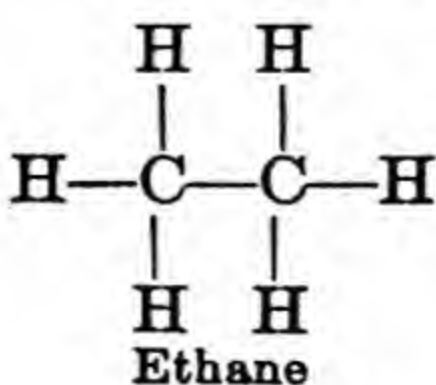
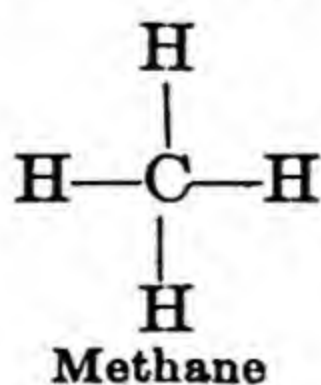
A line connecting two atoms is often used to represent a pair of shared electrons. These *structural* formulas show how the atoms are arranged in molecules. It is necessary to use structural formulas in dealing with compounds of carbon, for we often find two or more compounds to which the same ordinary formula must be assigned. For example, two very different compounds have the formula $\text{C}_2\text{H}_6\text{O}$. One of these compounds is ordinary ethyl alcohol, which boils at 78° and is soluble in water. The other is dimethyl ether, which is a colorless gas and insoluble in water. These two compounds have exactly the same composition and the same molecular weight. They have different properties because the atoms are arranged differently in the molecules of the two compounds. The following structural formulas show these different arrangements:



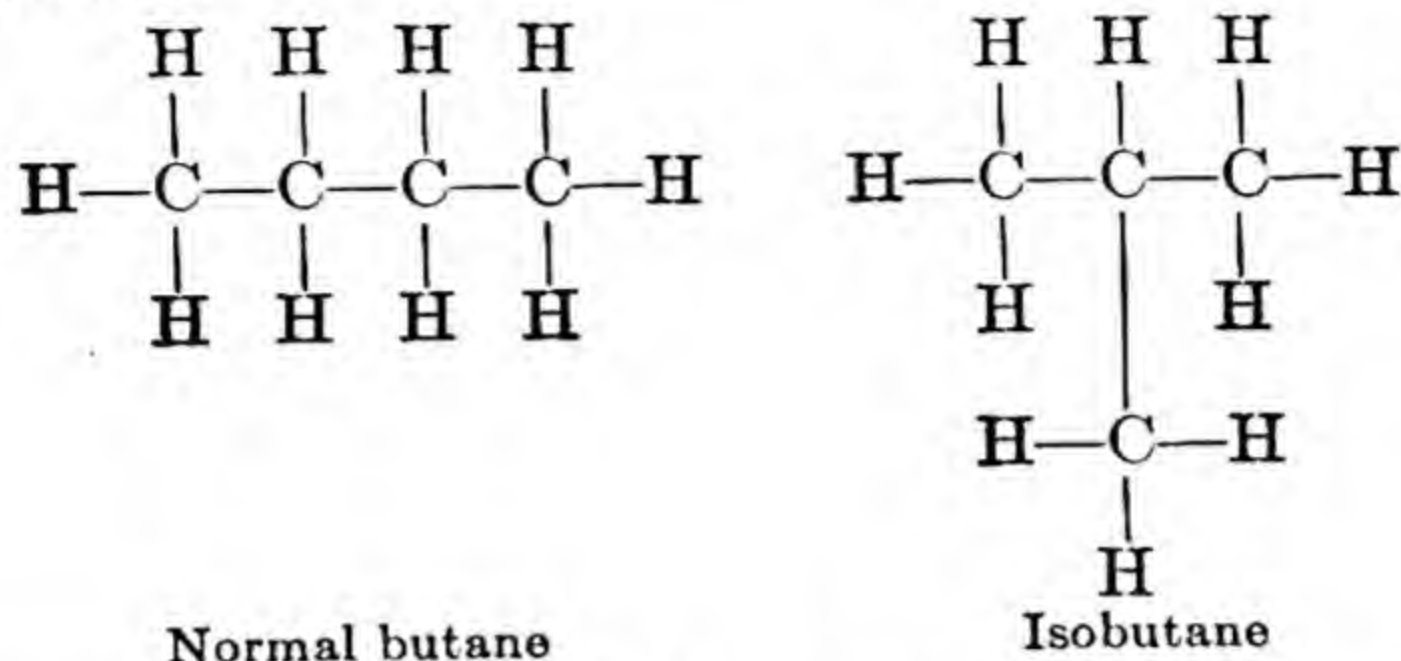
Compounds having the same composition and same molecular weight but differing in the arrangements of the atoms in the molecules are *isomers*.

Compounds composed of hydrogen and carbon only are called *hydrocarbons*. Gasoline, turpentine, benzene, and naphthalene are hydrocarbons. There are several classes or series of hydrocarbons, each class having some characteristic structural feature.

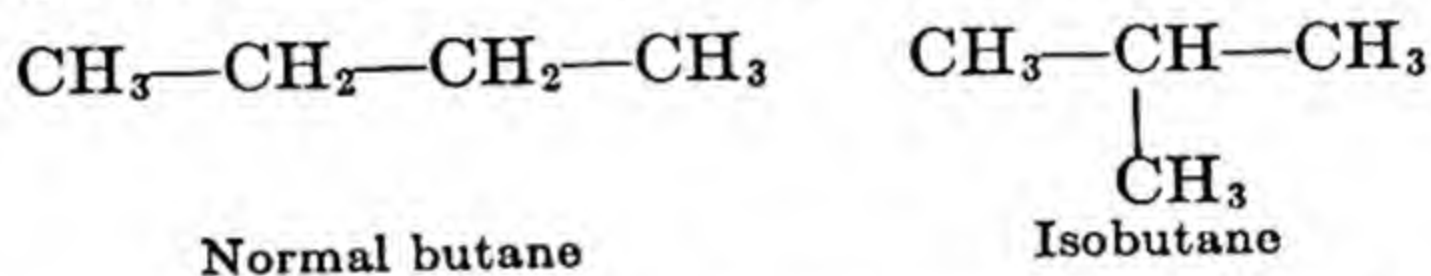
The alkane series. The first four members of the alkane series of hydrocarbons are colorless gases. They are known as methane, CH_4 ; ethane, C_2H_6 ; propane, C_3H_8 ; and butane, C_4H_{10} . Higher members are liquids or solids as indicated by the melting points shown in the table on page 462. The first three members are represented by the following structural formulas:



Isomerism and structure. There is only one possible way of arranging the atoms in either of the first three members of the series, but for the next member, butane, the two formulas shown below are possible.



Two butanes are known. They are called normal butane and isobutane. They have the same composition and same molecular weight, but possess different properties on account of the different structures of the molecules. The two structural formulas for butane may be written in a more condensed form as follows:



Isomers are common among carbon compounds and rare among compounds that do not contain carbon. As the number of carbon atoms in the molecule increases the number of possible isomers also increases. It is estimated that a hydrocarbon of this series containing 15 carbon atoms could have more than 4000 different arrangements of the atoms. In other words, it is possible, theoretically, to have more than 4000 different compounds corresponding to the formula $\text{C}_{15}\text{H}_{32}$. Only a few of these structures are known to exist. It might be possible to make them, but there is no incentive for such an effort.

Methane is one of the gases that escape from petroleum wells, and it is the principal component of the gas which bubbles from the water of swamps and marshes. It is formed wherever vegetable matter decays under water. It is commonly called *marsh gas* (coal miners call it fire damp), but its chemical name is methane. It sometimes issues from coal seams, filling the mine with an explosive mixture of methane and air, and many mine disasters have been traced to this cause. The frequency of such disasters was greatly reduced by the introduction of the miners' safety lamp, invented by Sir Humphry Davy. The products formed in such an explosion are carbon dioxide and water vapor. Natural gas is about 80 per cent methane.

ALKANE HYDROCARBONS*

Name	Formula	Melting point	Boiling point	Specific gravity
Methane.....	CH ₄	-184°	-161.4°	0.415 (at -164°)
Ethane.....	C ₂ H ₆	-172°	-88.3°	0.546 (at -88°)
Propane.....	C ₃ H ₈	-189°	-44.5°	0.585 (at -44.5°)
Butane.....	C ₄ H ₁₀	-135°	+0.6°	0.600 (at 0°)
Pentane.....	C ₅ H ₁₂	-131.5°	36.3°	0.627 (at 14°)
Hexane.....	C ₆ H ₁₄	-94.3°	69.0°	0.660 (at 20°)
Heptane.....	C ₇ H ₁₆	-90°	98.4°	0.683 (at 20°)
Octane.....	C ₈ H ₁₈	-56.5°	124.6°	0.702 (at 20°)
Nonane.....	C ₉ H ₂₀	-51°	150.6°	0.718 (at 20°)
Decane.....	C ₁₀ H ₂₂	-32°	174°	0.747 (at 0°)
Undecane.....	C ₁₁ H ₂₄	-26.5°	197°	0.773 (at m.p.)†
Dodecane.....	C ₁₂ H ₂₆	-12°	216°	0.774 (at m.p.)
Tetradecane.....	C ₁₄ H ₃₀	+5.5°	252.5°	0.775 (at m.p.)
Hexadecane.....	C ₁₆ H ₃₄	20°	287.5°	0.775 (at m.p.)

* The physical constants included in this table apply to the normal, or straight-chain, compounds
† m.p. = melting point.

General formulas. As we pass from one member of this series to the next, we see that there is an increase of one carbon atom and two hydrogen atoms in the molecule, or an increase of CH₂ in the formula. The general formula for the alkane series (saturated series) is C_nH_{2n+2}, if *n* is used to represent the number of carbon atoms in the molecule. For a hydrocarbon of this series containing 10 carbon atoms, the formula would be C₁₀H_{(2×10)+2} or C₁₀H₂₂.

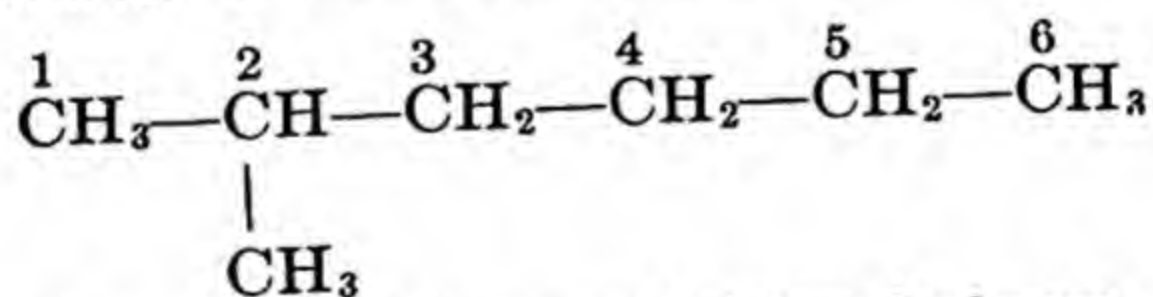
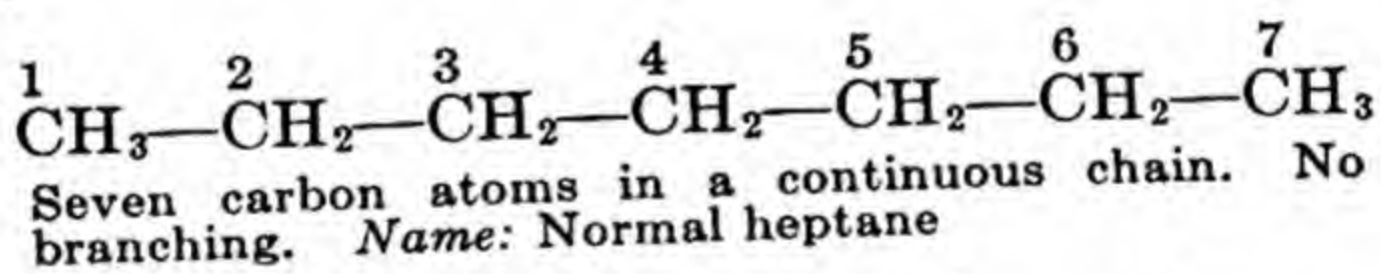
A group of atoms derived from a saturated hydrocarbon through the removal of one hydrogen atom is called an *alkyl radical*. It corresponds to the general formula C_nH_{2n+1}. The radical is named from the corresponding hydrocarbon by changing the final syllable of the hydrocarbon name from *ane* to *yl*.

Hydrocarbon	Alkyl Radical
CH ₄ = methane	—CH ₃ = methyl
C ₂ H ₆ = ethane	—C ₂ H ₅ = ethyl
C ₃ H ₈ = propane	—C ₃ H ₇ = propyl
C ₄ H ₁₀ = butane	—C ₄ H ₉ = butyl

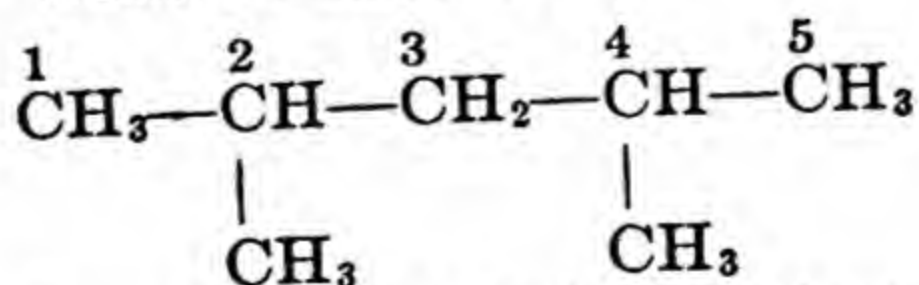
The alkyl radicals do not exist in the free state. They are always combined with other groups or with single atoms. Thus we have such compounds as methyl chloride, CH₃Cl, methyl alcohol, CH₃OH and acetic acid, CH₃COOH. In each of these compounds the alkyl radical, CH₃, is in combination with an atom or group of atoms. Similarly, we have ethyl chloride, C₂H₅Cl, ethyl alcohol, C₂H₅OH, and propionic acid, C₂H₅COOH, in each of which the ethyl radical appears.

It is customary to use the letter R as a symbol for any alkyl radical. The formula RCl stands for CH_3Cl , $\text{C}_2\text{H}_5\text{Cl}$, or any other compound in which an alkyl radical is combined with a chlorine atom. The formula CH_3Cl refers to one particular compound. It is a *specific formula*. On the other hand, RCl is a *general formula* which applies to any member of an entire class of compounds. Similarly, ROH is a general formula which stands for CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, or any other compound in which an alkyl radical is in combination with a hydroxyl group.

Nomenclature. The name of every compound in the alkane series of hydrocarbons ends in *ane*. The first part of the name, generally, indicates the number of carbon atoms in the molecule, but this practice does not apply to the first four members of the class. A modification of this rule is necessary if we want to assign distinguishing names to isomers. We have for example, nine heptanes, C_7H_{16} . There are nine possible ways of arranging seven carbon atoms and sixteen hydrogen atoms, using single points of attachment (no double bonds) and giving to each carbon atom a valence of four and to each hydrogen atom a valence of one. Each of these compounds is properly called a heptane, but in order to have a different name for each of the nine structures we base the name of each compound on the number of carbon atoms in the longest continuous chain of carbon atoms in the molecule. Let us consider the structures and names of three of the heptanes.



Seven carbon atoms and sixteen hydrogen atoms, therefore a heptane. Six carbon atoms in the longest continuous chain, therefore to be named as a derivative of hexane. A methyl group substituted for a hydrogen atom on carbon atom number 2. Name: 2-methyl-hexane.



Formula C_7H_{16} , therefore a heptane. Five carbon atoms in the longest chain, therefore to be named as a derivative of pentane. Name: 2-methyl-4-methyl-pentane.

Petroleum. Vast deposits of a mineral oil called *petroleum* have been located in many parts of the world. It is a dark-colored oily liquid composed principally of hydrocarbons. Light, colorless, liquid hydrocarbons are obtained from petroleum by fractional distillation. Fractional distillation is the process of separating a mixture into parts, or fractions, by distilling the mixture and collecting the parts of the distillate separately. Separation is



Courtesy, Brown Brothers

Fig. 173. "Drake's folly." The man with the tall hat is Mr. Drake.

possible because of the different boiling points of the substances in the mixture. The liquids with low boiling points pass off first from the mixture. Gasoline, which is a mixture of volatile hydrocarbons, was originally obtained exclusively by distilling crude petroleum. Now we supplement this method by the cracking process (page 465) and by condensation processes (page 466).

A mixture of liquid hydrocarbons less volatile than gasoline (distilling between 140° and 300°C.) is known as kerosene. Still heavier and less volatile liquid fractions of petroleum are used as lubricating oils. Petroleum contains many hydrocarbons which,

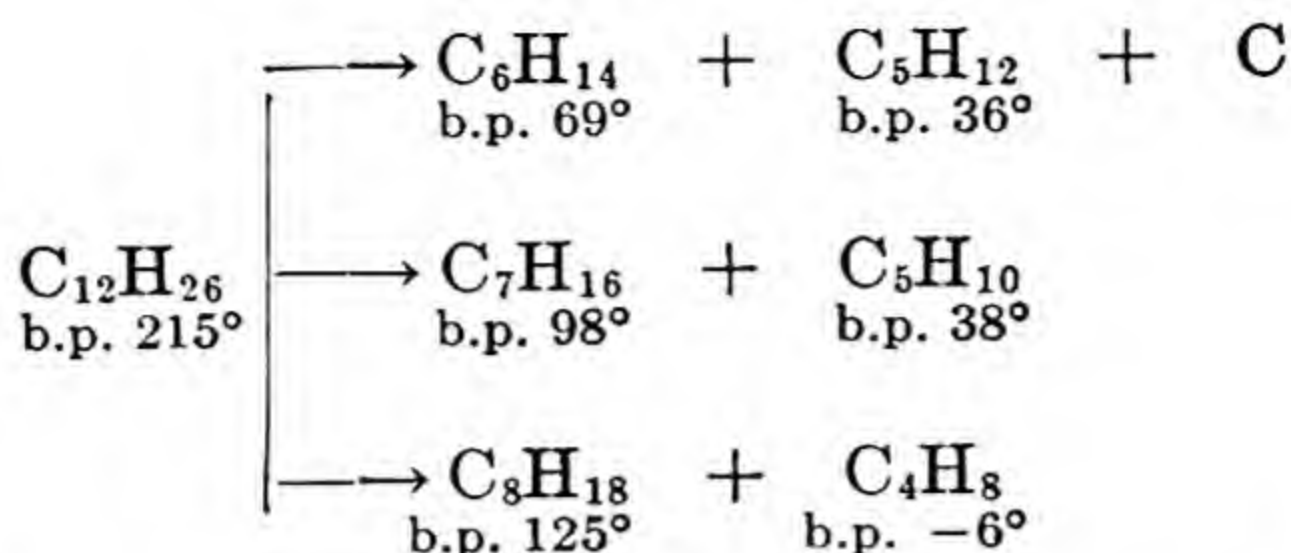
in the pure state, are solids. They are soluble in the liquid members of the mixture, but when the gasoline, kerosene, and lubricating oils have been distilled off, these components of petroleum appear as a solid residue. From this residue we obtain the greases used to lubricate bearings in all types of heavy machinery, and such products as vaseline, petrolatum, and paraffin wax.

Petroleum was used as a medicine by the Indians before Columbus discovered America. The oil oozed from the ground in several places in Pennsylvania and accumulated in small pools. The first successful attempt to tap an underground source of the oil was made at Titusville in 1859. Edwin Drake was employed by a small company of investors to try the experiment of drilling for oil, and the success of this venture started a new industry in this country. The site of "Drake's folly," as it was then called, is now a state park. Drake's well yielded 20 barrels of oil a day. The world production of petroleum is now approximately two billion barrels annually. In the United States, Texas leads with a yield of about 500,000,000 barrels a year. California produces nearly 600,000 barrels daily, and Oklahoma supplies about the same amount. The production of crude petroleum in one year in the United States has exceeded a billion barrels.

Improvements in refining methods have done much to reduce the waste of this valuable source of energy, and new synthetic processes have more than doubled the yields of desirable products. Among the more important developments in this field are (1) the cracking process, (2) condensation processes.

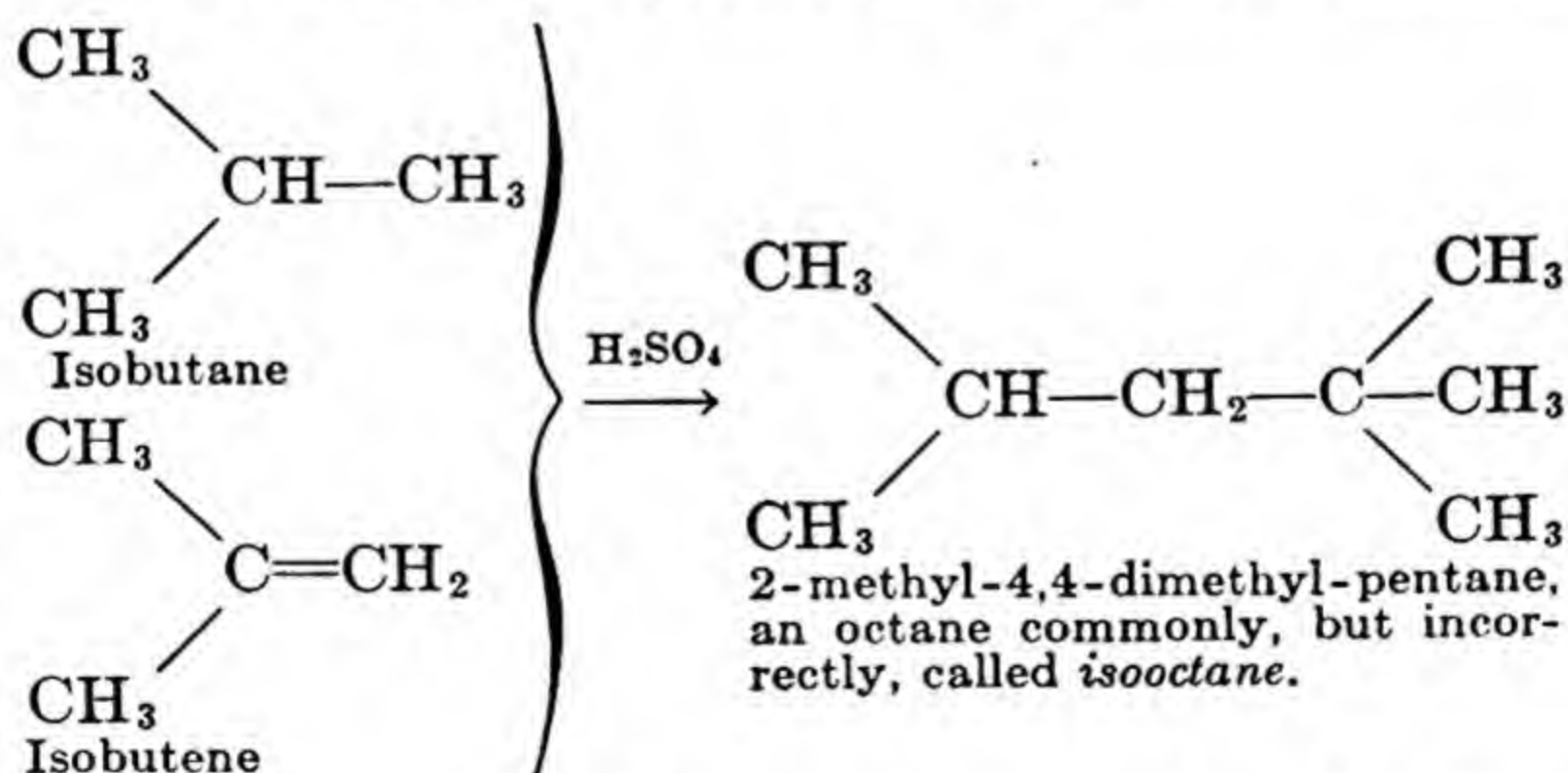
The cracking process. Gasoline is a mixture of hydrocarbons. It boils over the wide range of 85° to 200° and contains hydrocarbons of the alkane series ranging from pentane, C_5H_{12} , to undecane, $C_{11}H_{24}$. The principal components are hexanes, heptanes, and octanes. Hydrocarbons of higher molecular weights and higher boiling points are abundant in petroleum but not volatile enough to be useful in gasoline. These heavier compounds can be decomposed by heat with the production of light molecules—low-boiling liquids and gases. From these products good yields of gasoline may be obtained. The breaking of heavy hydrocarbons into lighter ones by heat is called a "cracking process."

High temperatures and high pressures are used to decompose the hydrocarbon oils, and mixed products are always obtained. Let us select one hydrocarbon, dodecane, from the dozens occurring in petroleum, and see what might happen to it at temperatures of 500° to 800° .



Many other results also are possible and to some extent they are realized. Each of these products, for example, exists in isomeric forms. Similar decompositions occur in all the components of the petroleum subjected to this treatment.

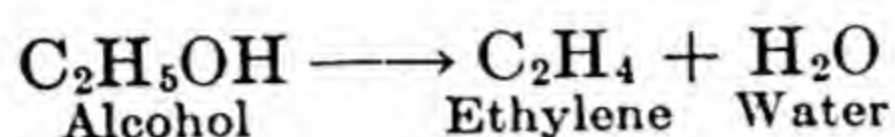
Condensation processes. Normal butane and isobutane, C_4H_{10} , are among the gases which escape from oil wells, and they are formed in the cracking of heavier hydrocarbons. Butene and isobutene, C_4H_8 , also are products of the cracking process. These are unsaturated hydrocarbons of the ethylene series. In the early days of the petroleum industry the butane and butene gases were waste products. Today there is an unlimited demand for isobutane and isobutene, for a method of making these two gases combine has been discovered and the main product formed from them is the octane which has proved to be the most valuable component of a high grade gasoline. The union of the two gases is called a *condensation process*. It is induced by contact with sulfuric acid which acts as a catalyst. Omitting the intermediate products formed, we may represent the condensation as follows:



Knocking in an automobile engine may be due to premature explosions of the fuel gases in the cylinders or to the explosion wave proceeding at too high a velocity. Both causes of knocking can be overcome by increasing the percentage of this branched-chain octane in the gasoline or by adding to the gasoline a very small quantity of the poisonous liquid lead tetraethyl, $\text{Pb}(\text{C}_2\text{H}_5)_4$.

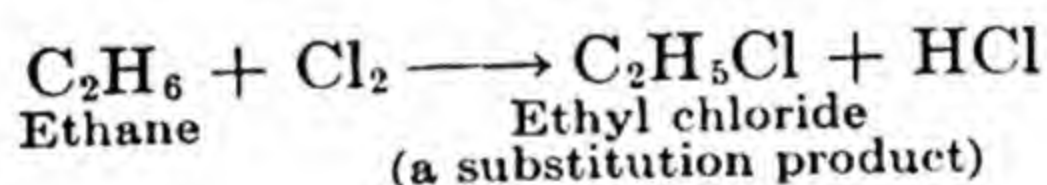
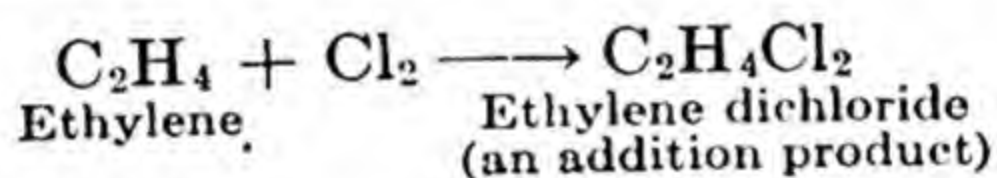
The alkene series. When ordinary alcohol and sulfuric acid are heated together, a colorless gas is liberated which has the

formula C_2H_4 . It is called *ethene* or *ethylene*. The gas may be made also by passing alcohol vapor over hot aluminum oxide or thorium oxide. The net result of either process is indicated by the equation:

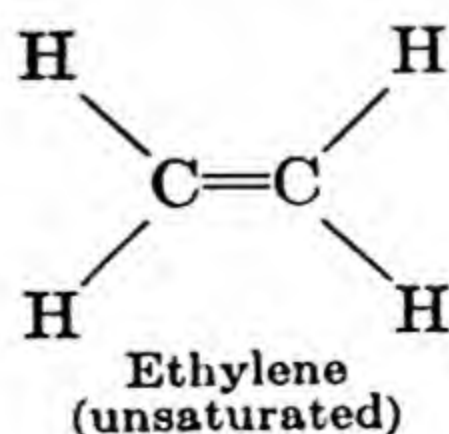
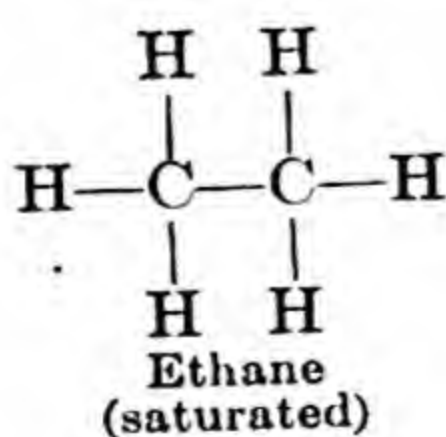


The general formula for hydrocarbons of the alkene or ethylene series is C_nH_{2n} . If we compare the formula of ethylene with that of ethane, we see that the two formulas differ by two hydrogen atoms, and this difference in composition is accompanied by great differences in chemical reactivities. Ethylene combines readily with chlorine and bromine, forming $C_2H_4Cl_2$ and $C_2H_4Br_2$, respectively. These are called *addition products*, for in them we have the reagents chlorine, and bromine in addition to the original ethylene molecules.

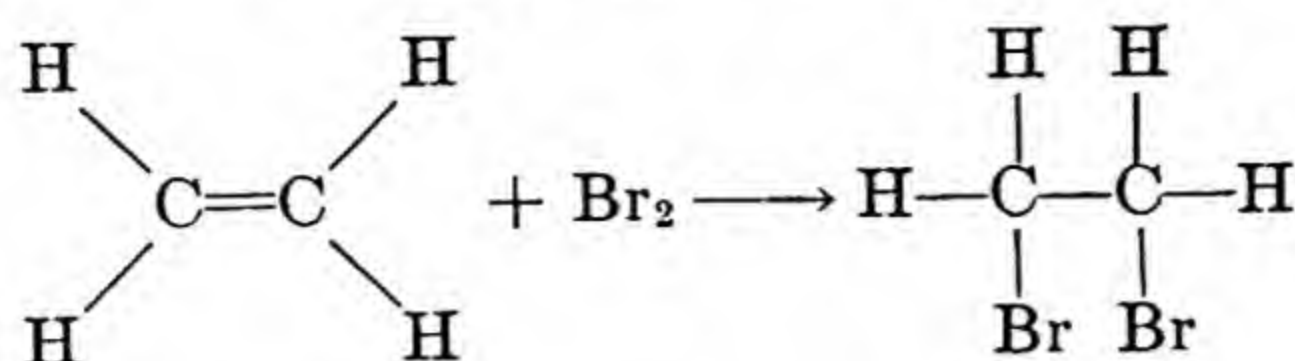
Saturated hydrocarbons do not form addition products. Let us compare, for example, the action of chlorine on ethylene and ethane. The compounds react as follows:



Since ethylene forms addition products readily, it is said to be *unsaturated*; and since ethane fails to form an addition product, it is classified as a *saturated* compound. The action of ethylene is explained by the assumption that, in this compound, there is a double bond between the two carbon atoms. This double bond is easily broken and atoms like chlorine, or radicals like the hydroxyl group, can add to the unsaturated molecule. Saturated compounds have single bonds only between carbon atoms. The structural formulas for ethane and ethylene are written as follows:

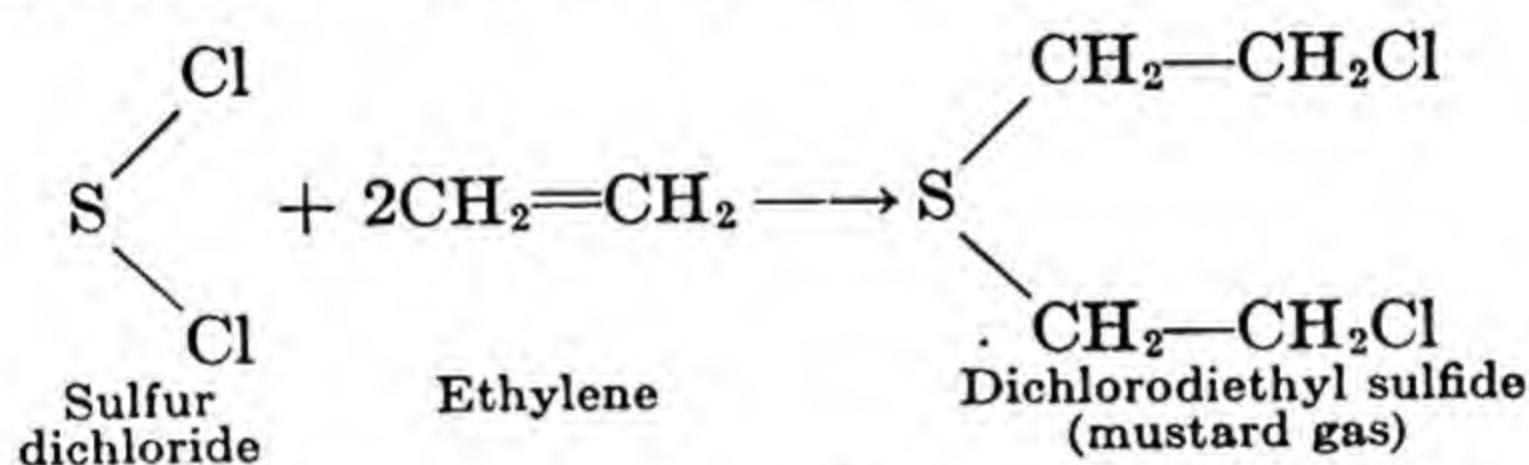


The reaction between ethylene and bromine is represented as follows:



Ethylene is a colorless gas with a sweet odor. It burns with a luminous flame, and is often added to natural gas supplies to make the flame visible. It is used also as an anesthetic for dental and general surgery. The gas is inhaled with oxygen. Recovery of the patient from the anesthesia is rapid.

Ethylene is employed in the production of mustard gas, one of the weapons of modern warfare. Although commonly called mustard gas, the compound is a liquid which boils at 216° . The liquid, in contact with the skin, causes burns, and the vapor, if inhaled, destroys the lung tissues and acts as a poison. Mustard gas is made by passing ethylene gas into a solution of sulfur dichloride in carbon tetrachloride.



There are many unsaturated hydrocarbons each of which, like ethylene, has a double bond between carbon atoms. The lower members are gases and the higher members are liquids or solids. The name-ending for a hydrocarbon of this series is *ene* or *ylene*. A few members of the series are listed below.

Name	Formula	Boiling Point
Ethylene (ethene).....	$\text{CH}_2=\text{CH}_2$	-103.8°
Propylene (propene).....	$\text{CH}_3-\text{CH}=\text{CH}_2$	-47.0°
Butylene (butene):		
Ethylethylene (1-butene).....	$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	-18.0°
Sym. dimethylethylene (2-butene).....	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$	$+1.4^\circ$
Isobutylene (2-methyl-propene).....	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	-6.0°
Octylene (normal) (1-octene).....	$\text{C}_6\text{H}_{13}-\text{CH}=\text{CH}_2$	$+123.0^\circ$
Decylene (normal) (decene).....	$\text{C}_8\text{H}_{17}-\text{CH}=\text{CH}_2$	$+172.0^\circ$

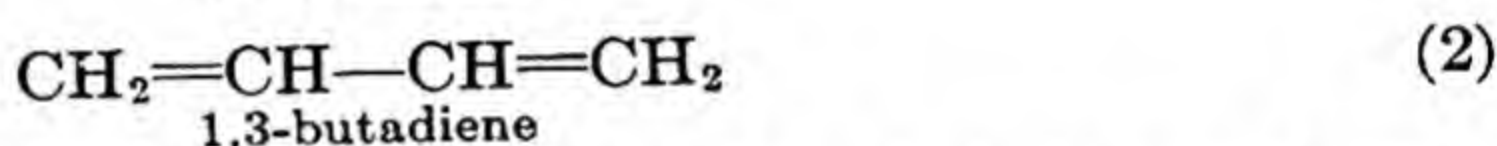
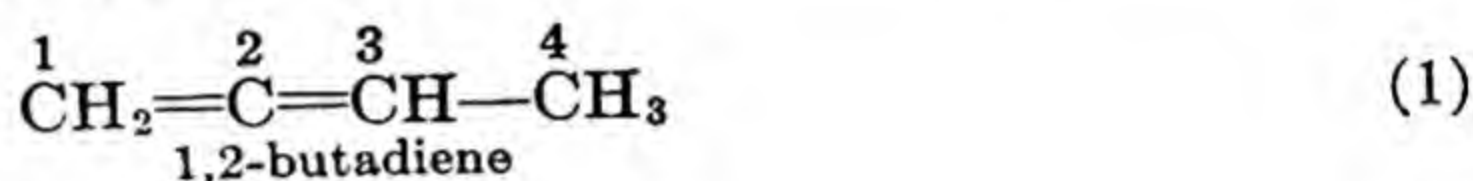
There is only one ethylene and one propylene, but there are three butylenes (or butenes) as indicated in the table. There are five amylenes or pentenes and many more isomers of compounds

having higher molecular weights. The isomerism in this series is due not only to branching in the carbon chains but also to changes in the position of the double bond. The position of the double bond is indicated by a number preceding the name of the compound. The structure



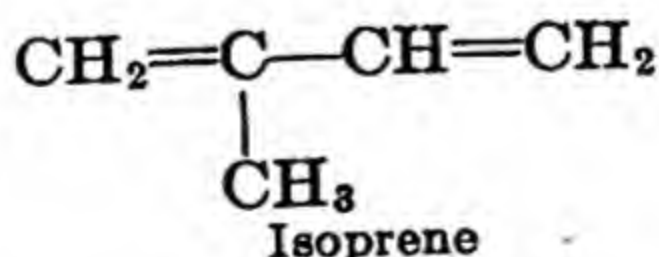
is 2-pentene, the suffix *ene* indicating the presence of a double bond and the numeral indicating that the double bond constitutes the second carbon-to-carbon linkage in the chain.

The dienes. A compound having two double bonds in the molecule is called a diene (*dī'-ēēn*). We have, for example, two compounds corresponding to the molecular formula C_4H_6 . They have the following structures:



The suffix *diene* means there are two double bonds in the molecule. In formula (1) these double bonds constitute the first and second carbon-to-carbon linkages. In formula (2) the double bonds are in the first and third positions. One of these compounds (2) is now being made in enormous quantities for use in the manufacture of rubber.

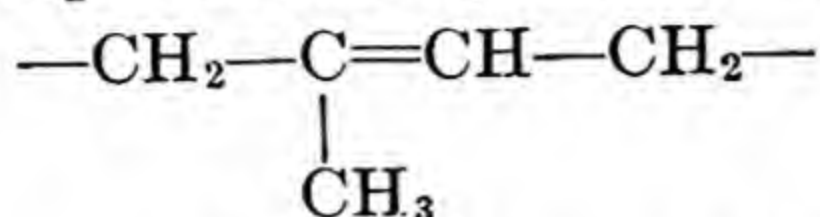
Natural rubber is obtained from a milky emulsion that drips from certain tropical trees when a segment of bark is cut away. The composition of natural rubber is represented by the formula $(\text{C}_5\text{H}_8)_n$ in which n stands for a large but indefinite number. The unit C_5H_8 is an unsaturated hydrocarbon, called *isoprene*, or 2-methyl-1,3-butadiene. It has the following structural formula:



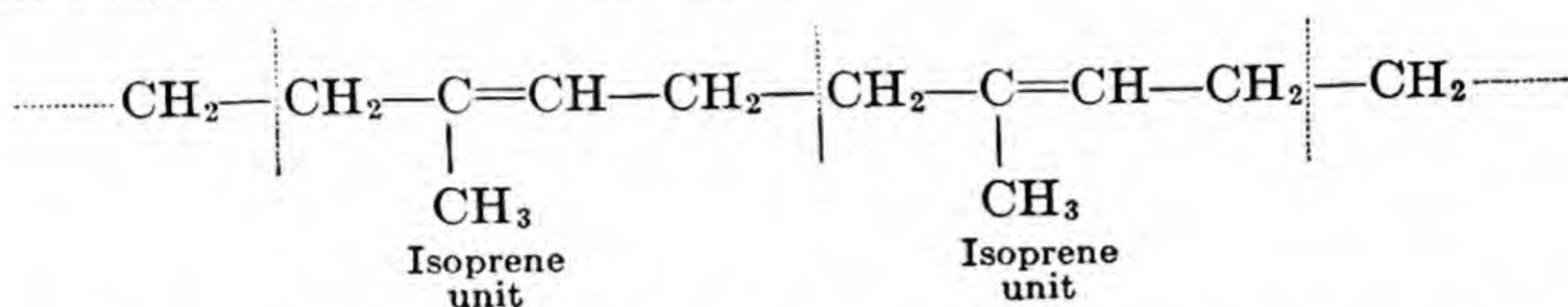
Isoprene is a colorless liquid which boils at 34° . It is insoluble in water, but soluble in all proportions in alcohol and in ether. Metallic sodium catalyzes the polymerization of isoprene, producing a substance which closely resembles natural rubber.

Polymerization is a process in which two or more molecules of the same kind unite to form larger molecules without change in composition. The larger molecules are called *polymers* of the original compound. Rubber is a polymer of isoprene. The rubber

molecule consists of a long chain of isoprene units. Disregarding the intermediate products formed with the sodium or other catalyst, we may assume that the isoprene molecules are brought into the active state represented by the following structure:



Units of this kind can combine to form molecules of great length. The molecular weight of rubber is at least 100,000, which means that more than 1400 isoprene molecules combine to form a single molecule of rubber. The formula for a section of a rubber molecule may be written in this form:

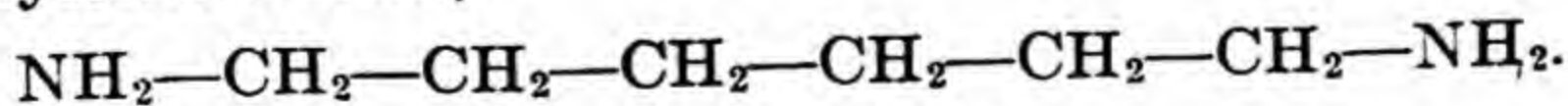


At each end of the molecule there must be an extra atom of hydrogen or some other element to satisfy the valence requirements of the terminal carbon atoms.

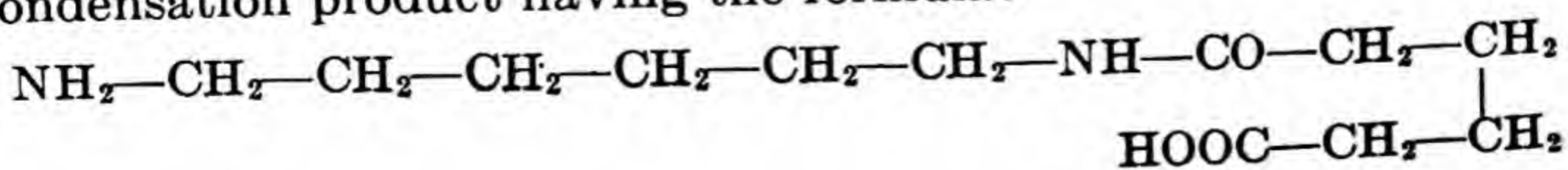
1,3-butadiene, $\text{CH}_2=\text{CH—CH=CH}_2$, a colorless gas which can be made from petroleum, from alcohol, or from acetylene, is one of the most useful hydrocarbons available for the manufacture of elastomers (artificial rubbers).

Butadiene and an unsaturated compound called styrene, $\text{C}_6\text{H}_5\text{—CH=CH}_2$, are polymerized together to form the rubber known as buna-S (*bu* for butadiene, *na* for sodium, and *S* for styrene—the three substances originally used in the synthesis of this type of rubber).

Nylon. Synthetic silk is not a hydrocarbon product, but it deserves brief mention here, for it is another example of long chain molecules produced by the condensation of simple compounds. The principal reagents used in making nylon are adipic acid, $\text{COOH—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—COOH}$, and an amine called hexamethylenediamine,



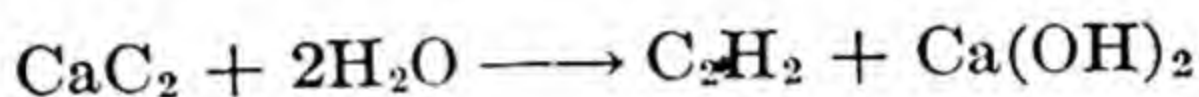
A carboxyl group, COOH , of the acid, reacts with an amino group, NH_2 , of the amine, eliminating a molecule of water and forming a condensation product having the formula:



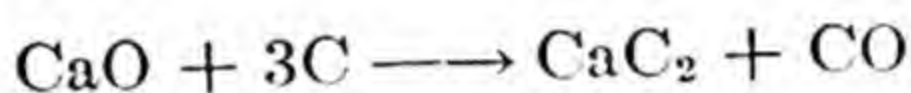
This product can combine with another amine molecule through the COOH group at one end of the chain or with another adipic acid molecule through the NH₂ group at the opposite end of the chain. Under proper laboratory conditions this type of condensation can be made to continue until a molecule of enormous size has been formed. From these long molecules artificial silk is made. Nylon closely resembles natural silk in texture, lightness, and strength.

The alkyne series. *Acetylene.* Before electric lights were available, the best artificial light was produced by burning acetylene gas. A dazzling white light is produced when acetylene burns in oxygen, and the flame (oxyacetylene flame) attains a temperature high enough to melt iron rapidly.

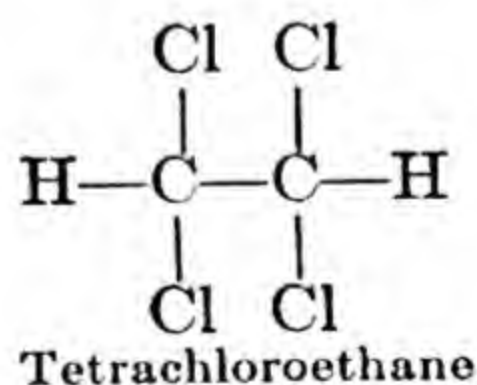
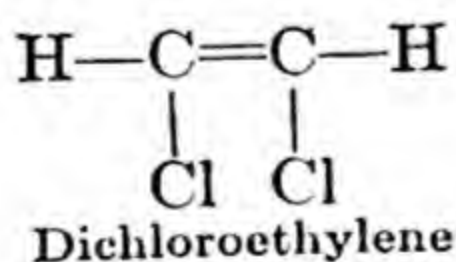
Acetylene has the formula C₂H₂. It is made by dropping water onto powdered calcium carbide:



Calcium carbide, a gray powder having the formula CaC₂, is made by heating a mixture of lime and coke in an electric furnace:



Acetylene combines readily with chlorine, forming compounds having the formulas C₂H₂Cl₂ and C₂H₂Cl₄. We conclude, therefore, that acetylene is even more unsaturated than ethylene, and we assume that the two carbon atoms are joined by a triple bond. When acetylene reacts with chlorine, these extra bonds are broken. The first addition of chlorine produces dichloroethylene, and the second addition of Cl₂ produces the saturated compound tetrachloroethane.

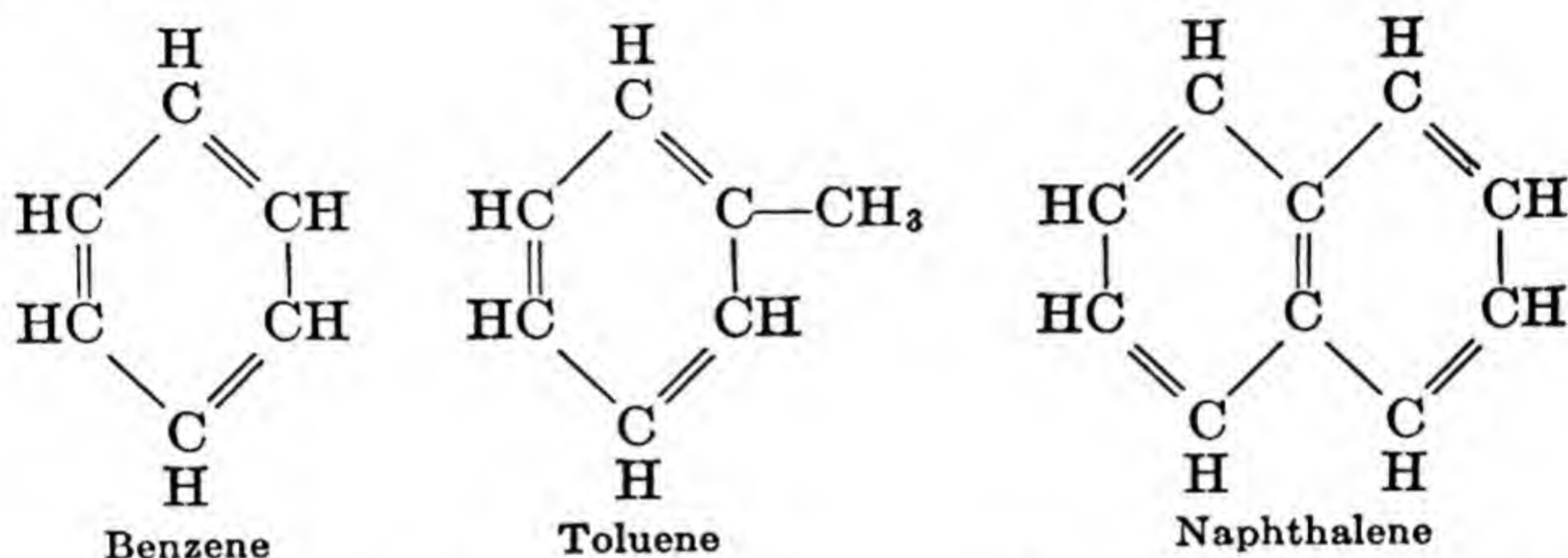


Members of the alkyne or acetylene series of compounds have the general formula, C_nH_{2n-2}. The first member is by far the most important one.

Acetylene has a disagreeable odor when prepared from calcium carbide, but is practically odorless when it has been purified. It is colorless, somewhat poisonous, sparingly soluble in water, but extremely soluble in acetone. Acetylene is used for cutting and welding metals, and as a source of illumination.

The aromatic series. When coal is heated in the absence of air, combustible gases escape at first; then a viscous black liquid (coal tar) distills out of the mass and a residue of coke remains in the retort. Benzene, C_6H_6 , is obtained from the tar by a process known as fractional distillation. Benzene is a colorless liquid which boils at $80.4^\circ C$. and freezes to a crystalline solid at $5.4^\circ C$. It is an excellent solvent for fats and oils.

In the benzene molecule the six carbon atoms are arranged in a closed chain or *ring*, as shown in the structural formula below. *Toluene*, the second member of the aromatic series, has the formula $C_6H_5-CH_3$. *Naphthalene*, $C_{10}H_8$, a colorless solid hydrocarbon which is used as moth balls, has two closed chains of atoms in the molecule.



Compounds like benzene, toluene, and naphthalene having ring structures are called *aromatic* compounds, and those having open chains of carbon atoms are called *aliphatic* compounds. *Benzene* is a pure chemical compound belonging to the aromatic series of hydrocarbons, but *benzine* is a mixture of pentane, hexane, and some other hydrocarbons of the aliphatic series. Benzene is obtained from coal tar; benzine is obtained from petroleum. The two names are pronounced alike but spelled differently.

The members of the benzene series and their derivatives are used in the manufacture of coal-tar dyes, high explosives, drugs, and many other useful products. Naphthalene, in addition to its use in moth balls, is used also in the preparation of smokeless powders and in the manufacture of celluloid.

Questions and Exercises

1. What is petroleum?
2. Name three hydrocarbons of the alkane series.
3. Name three commercial products that are composed of mixed hydrocarbons.
4. Write a balanced equation representing the explosion of a mixture of ethane and air.

5. What volume of acetylene (at 0°C. and 76 cm. pressure) can be made by the action of water on 50 g. of calcium carbide?

6. How many liters of air will be required for the complete combustion of 10 liters of propane? The products are carbon dioxide and water. Assume that all gases are measured under standard conditions of temperature and pressure.

7. Write a general formula for each of the three series of aliphatic hydrocarbons.

8. Write a structural formula for (a) methane, (b) butane, (c) ethylene, and (d) acetylene.

9. What are isomers?

10. Draw the structural formulas for two isomers of butane.

11. How many structural formulas can you draw for the isomers of pentane? (Three are possible.)

12. Explain why there are so many hydrocarbons.

13. Why do we say that ethylene and acetylene are "unsaturated" hydrocarbons?

14. Name three uses for members of the aromatic series of hydrocarbons.

15. Draw a structural formula for benzene.

PART 2

Halogen Compounds and Alcohols

Halogen Compounds

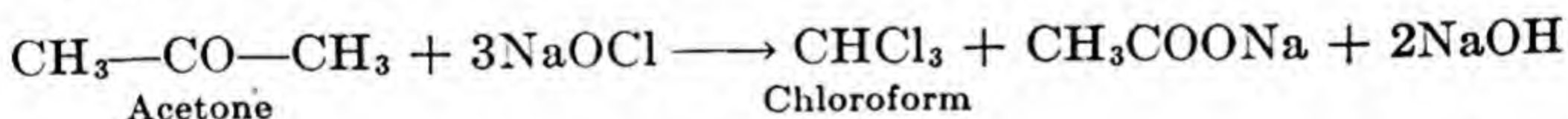
A large number of compounds may be formed from hydrocarbons by the substitution of other elements (or radicals) for hydrogen atoms. Many of these are important in everyday life. We shall study a few of them.

There are four possible chlorine substitution products of methane:

- CH_3Cl — monochloromethane (methyl chloride)
- CH_2Cl_2 — dichloromethane (methylene chloride)
- CHCl_3 — trichloromethane (chloroform)
- CCl_4 — tetrachloromethane (carbon tetrachloride)

It is possible to make all these compounds through the direct action of chlorine on methane, but it is not a simple matter to get a single pure product in this way. Better methods are available for making each of these halogen compounds.

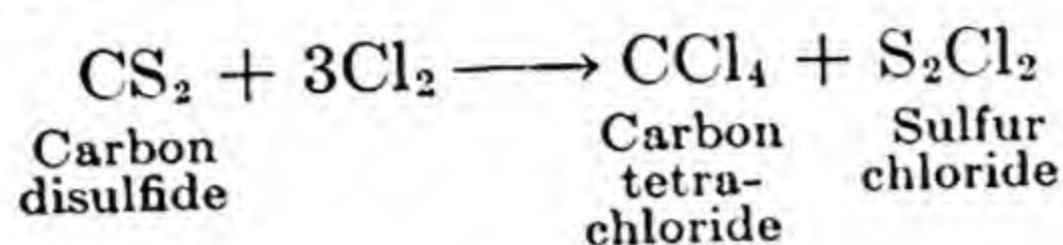
Chloroform. On a small scale chloroform is made from alcohol or acetone by treatment with sodium hypochlorite:



In larger quantities it is made by reducing carbon tetrachloride with iron and steam. Chloroform is a heavy, colorless liquid which boils at 61.2°C . It is an excellent solvent for fats, oils, and resins. It was formerly used extensively as an anesthetic, but in view of its detrimental action on the heart it has been replaced, in this capacity, by safer compounds such as ether and ethylene.

Carbon tetrachloride. This compound is a noninflammable, colorless liquid having a low boiling point. It is a solvent for grease and fat, and since it will not burn, it is a safe liquid for use in dry cleaning. It is used also in one type of fire extinguisher. When it is sprayed on a fire, it vaporizes, forming a heavy gas over the burning object. It thus prevents oxygen from reaching the

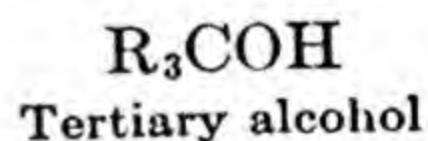
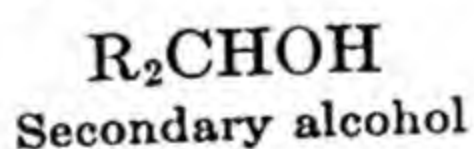
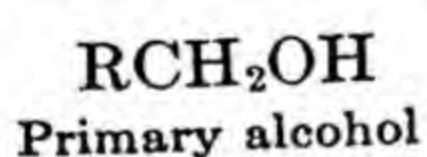
object, and the fire is extinguished. There is a little danger in the use of carbon tetrachloride as a fire extinguisher, for at high temperatures it is oxidized by air to form phosgene gas, COCl_2 , which is a very poisonous compound. Carbon tetrachloride is made from chlorine and carbon disulfide:



Iodoform. A compound corresponding to the formula CHI_3 is prepared by the action of iodine and alkali on alcohol. It is a yellow powder having a strong odor and valuable antiseptic properties.

Alcohols

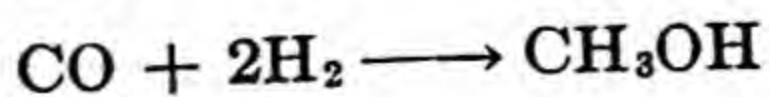
An alcohol is a substitution product of a hydrocarbon in which a hydrogen atom of the hydrocarbon has been replaced by a hydroxyl group. There are three classes of alcohols: primary, secondary, and tertiary. In a primary alcohol the hydroxyl group is attached to a carbon atom which is directly attached to not more than one other carbon atom. In a secondary alcohol the hydroxyl group is held by a carbon atom which is linked to two other carbon atoms; and in a tertiary alcohol the hydroxyl group is held by a carbon atom which is directly attached to three other carbon atoms. The general formulas are:



The term *alcohol*, like the term *salt*, is not a name for a specific compound but the name of a class of compounds. We often use the word "salt" when we mean sodium chloride, and in the same way we use the word "alcohol" when we mean *ethyl alcohol*. Every alcohol has at least one hydroxyl group (OH) attached to carbon.

Methyl alcohol. Methyl alcohol, CH_3OH , is known also as *methanol* or *wood alcohol*. It is one of the volatile products formed when wood is distilled. To obtain it, wood is heated in a retort from which air is excluded. If air were admitted to the retort, ordinary combustion would occur.

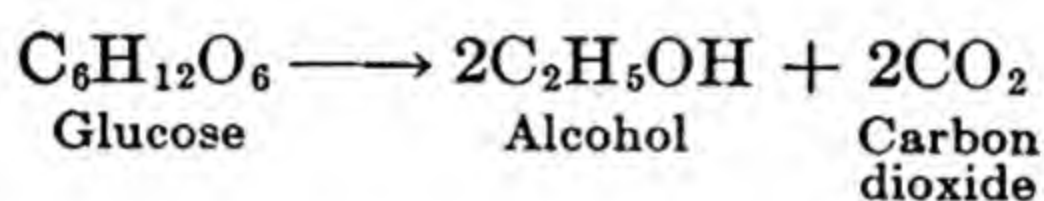
Methyl alcohol is made also from carbon monoxide and hydrogen by heating a mixture of the two gases in contact with a catalyst, and under high pressure:



The catalyst commonly used is a mixture of oxides of zinc, copper, and chromium.

Methyl alcohol is a colorless liquid which boils at 64.5°C. and is soluble in water in all proportions. It burns in air with a hot, nonluminous flame, the products of combustion being carbon dioxide and water. It is used in large quantities in the chemical industries as a solvent for fats, waxes, resins, and other organic substances. It is an active poison, and blindness is one of the physiological effects produced by drinking methyl alcohol or by inhaling its vapor.

Ethyl alcohol. Ethyl alcohol, C_2H_5OH (grain alcohol), is made from glucose, $C_6H_{12}O_6$, or from cane sugar, $C_{12}H_{22}O_{11}$, by fermentation. Fermentation is induced by an enzyme found in yeast. An enzyme is a chemical compound which is derived from living cells and which is capable of catalyzing a chemical reaction. When yeast is added to a warm solution of glucose the following change occurs:



Cane sugar also is fermentable, and alcohol is made from molasses, which is a by-product in the process of refining sugar.

Any source of starch can be utilized in the manufacture of alcohol, for when malt is added to starch and the mixture is placed in warm water, the starch is gradually converted into a fermentable sugar. Malt is made from barley by keeping the grain warm and moist until it begins to grow. The sprouting barley contains a chemical substance (an enzyme) which is capable of inducing a reaction between starch and water. Through this reaction (hydrolysis) the starch is changed to a sugar called *maltose*. Yeast is then added. Yeast supplies at least two enzymes. One of these enzymes induces the hydrolysis of maltose to glucose, and a different enzyme causes the fermentation of the glucose. All these reactions are carried out in water, and the alcohol obtained in this way is freed from the water by fractional distillation. Fusel oil, a by-product of the fermentation process, is composed of alcohols that are much more poisonous than ethyl alcohol. Pure ethyl alcohol is a colorless liquid that boils at 78.3°C. and dissolves in water in all proportions.

Millions of gallons of alcohol are used annually in industrial processes. As a solvent, ethyl alcohol stands next to water in commercial importance. The manufacture of celluloid products depends upon the use of alcohol or ether as a solvent, and ether is

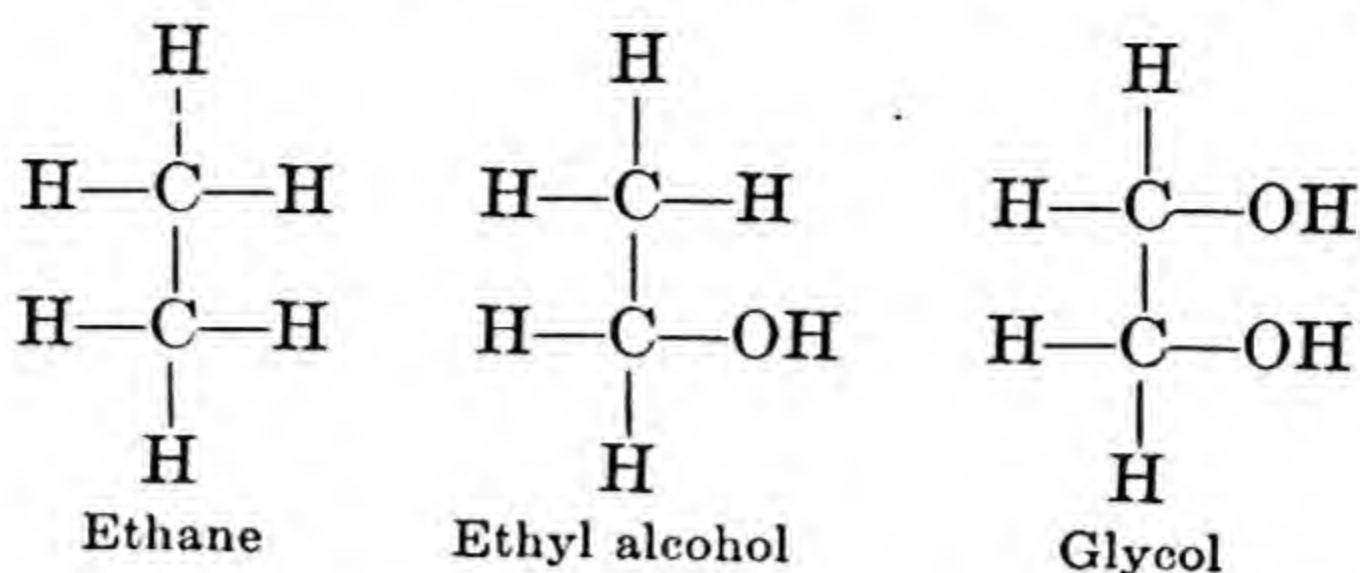
made from alcohol. Photographic films, artificial silk, transparent soap, vinegar, artificial flavors, perfumes, and many drugs and dyes are made by processes requiring the use of alcohol. Alcohol is used as a solvent, or as a chemical source of required materials, in the preparation of the lacquers used on airplane wings and on automobiles, it is equally valuable in the manufacture of smokeless powders, percussion caps and several other explosives. Alcohol is an important source of butadiene which, in turn, is used in the manufacture of rubber.

In order to provide alcohol for industrial use at a moderate price, the government permits the sale of denatured alcohol tax-free. It is denatured by adding to it substances which render the alcohol unfit for use in beverages but which are not detrimental to its industrial application. Among the compounds used for this purpose are pyridine, a vile-smelling liquid, and methanol (wood alcohol).

Alcohol has been used in beverages from the earliest period of written history. Fruit juices contain the sugar necessary for the fermentation process, and yeasts which yield the enzymes necessary for fermentation are found almost everywhere. In warm climates fermentation begins in a short time when fruit juices are allowed to stand in open containers. This spontaneous fermentation accounts for the early discovery of wine. Yeast is killed by alcohol if the concentration exceeds 17 per cent. Wines like sherry and port, with 20 per cent alcohol by volume, are fortified; that is, they contain more alcohol than could be produced from the grape juice by fermentation alone. Whiskey, brandy, rum, and gin are distilled liquors containing approximately 40 per cent alcohol.

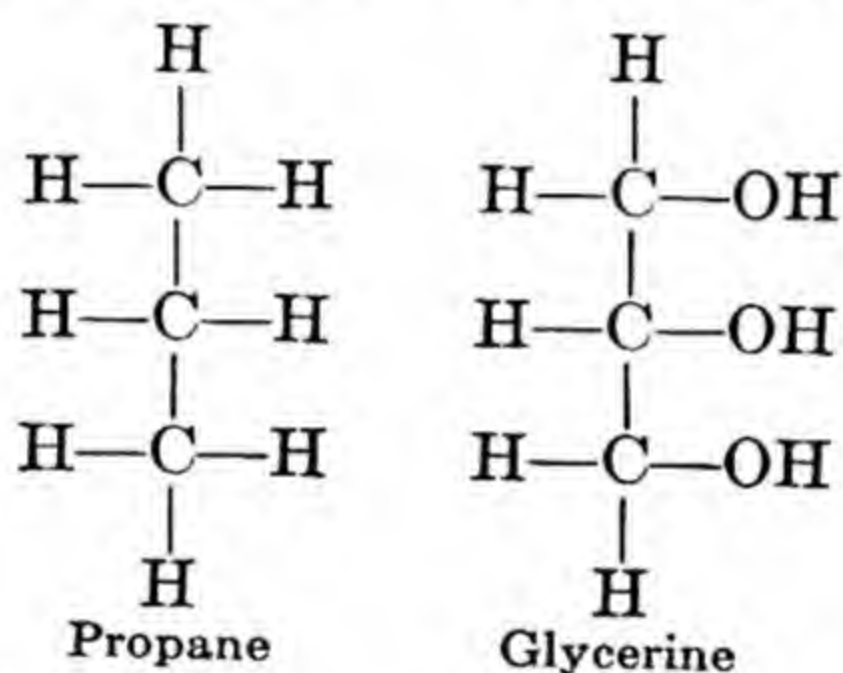
By distillation it is possible to obtain 95 per cent alcohol. When *absolute alcohol* (100 per cent alcohol) is required, the last 5 per cent of water is removed by treatment with lime or by distillation with benzene. A mixture of alcohol, water, and benzene boils at 64.9°C. as long as the three components are present. The composition of the distillate from the mixture is benzene 74.1 per cent, alcohol 18.5 per cent, and water 7.4 per cent. When all the water has been distilled out the temperature of the boiling mixture of benzene and alcohol rises to 68.2°C. The distillate from this constant-boiling mixture is 67.6 per cent benzene and 32.4 per cent alcohol. When the benzene has distilled out the temperature rises to 78.3°, which is the boiling point of pure alcohol.

Glycol. An alcohol containing two hydroxyl groups and having the formula $C_2H_6O_2$ is known as glycol. Its relationship to the hydrocarbon ethane and to ordinary ethyl alcohol is indicated by the following structural formulas:



Glycol is a colorless liquid which boils at 197.5°C . and freezes at -15.6°C . A solution of glycol in water is used sometimes in automobile radiators in cold climates. The solution freezes at a temperature several degrees below the freezing point of pure water.

Glycerine. Glycerol, commonly called glycerine, is an alcohol containing three hydroxyl groups in each molecule. It is related to the hydrocarbon propane, as indicated by the following formulas:

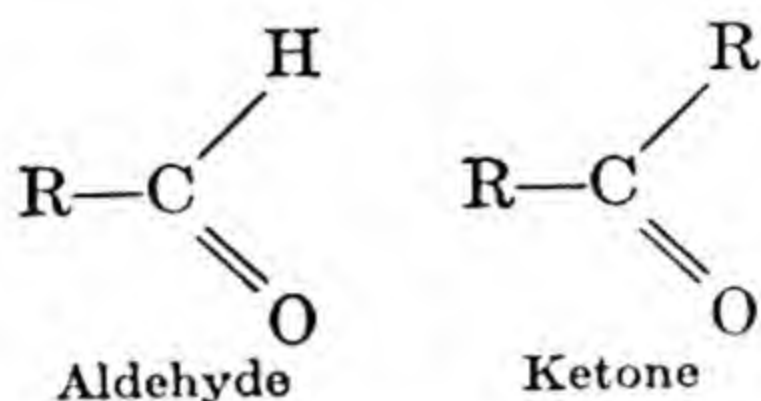


Glycerine is a heavy, colorless liquid, soluble in water, and having a sweet taste. We obtain glycerine from animal and vegetable fats and oils. It does not exist in the free state in fats and oils, but is formed when these substances are boiled with alkalies, as for example in the process of making soap. Glycerine is a by-product of the soap factory. It is used in the manufacture of nitroglycerine for dynamite, and in the preparation of certain kinds of plastics and toilet preparations.

PART 3

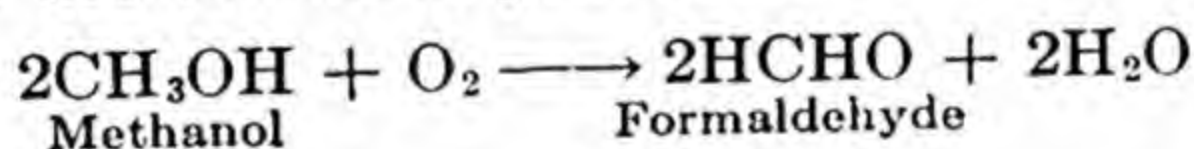
Aldehydes, Ketones, and Acids

Aldehydes and ketones are represented by the following general formulas:



In these formulas R stands for a carbon radical. (In the exceptional case of formaldehyde R stands for a hydrogen atom.) Aldehydes may be made from primary alcohols and ketones from secondary alcohols by oxidation processes.

Formic aldehyde, formaldehyde. This product is obtained through the oxidation of methanol or wood alcohol. When methyl alcohol vapor and air are passed over a hot copper gauze, formaldehyde and water are the main products:



Formaldehyde is a gas that is very soluble in water. Formalin, a 40 per cent solution of formaldehyde in water, is used as a preservative for anatomical specimens in laboratories and museums. Formaldehyde is used extensively in the manufacture of plastics. It combines with phenol (carbolic acid) to form a substance similar to hard rubber. We use more than 30,000,000 pounds of formaldehyde annually for this purpose alone. The phenol-formaldehyde plastics are sold under various trade names, including *bakelite*, *textolite*, and *formica*. Bakelite is used as an insulation for telephone switchboards and in making structural parts of other electrical appliances. Many phonograph records, fountain pens, clock cases, and umbrella handles are made of the same material. Formaldehyde is used with urea and with casein to make other types of plastic materials. Lamp shades, radio housings, buttons, billiard balls, tableware, jar caps, instrument dials, belt buckles, and beads are among the common articles made of these plastics.

Acetaldehyde. Ordinary ethyl alcohol can be oxidized in two stages to yield either acetaldehyde or acetic acid:

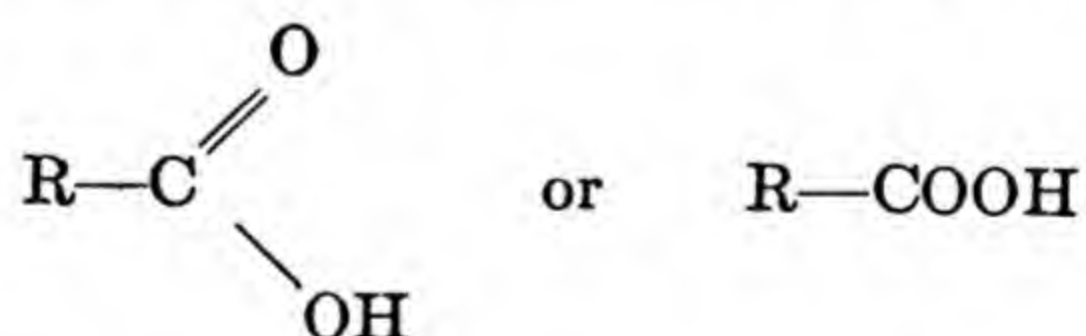


Acetaldehyde is a colorless, inflammable liquid which boils at 21°. It is soluble in all proportions in water, alcohol, and ether.

Acetone. The simplest ketone is acetone, CH_3COCH_3 , a colorless liquid which boils at 56.5°. It is one of the products formed in the destructive distillation of wood. It is made also by the thermal decomposition of sodium acetate, and by a fermentation process. Acetone is a very valuable solvent for resins used in varnishes and lacquers. A common example of its solvent action is its use as a fingernail polish remover.

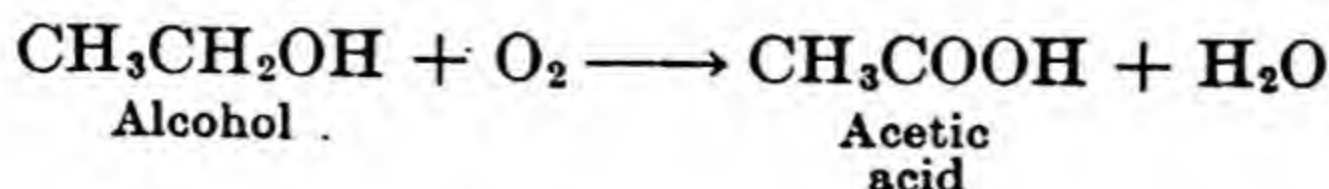
Acids

Organic acids are found in many fruits and vegetables. Citric acid, $\text{C}_6\text{H}_8\text{O}_7$, occurs in lemons, oranges, raspberries, currants, gooseberries, and many other fruits. It is a crystalline solid which melts at 100°C. Oxalic acid, $\text{C}_2\text{H}_2\text{O}_4$, is found in rhubarb; malic acid, $\text{C}_4\text{H}_6\text{O}_5$, occurs in green apples; and tartaric acid, $\text{C}_4\text{H}_6\text{O}_6$, is obtained from grapes. Lactic acid, $\text{CH}_3\text{—CHOH—COOH}$, gives the characteristic taste to sour milk. A great majority of the organic acids contain the group —COOH , which is called the *carboxyl* group. The general formula for an acid is:



Formic acid. In formic acid, HCOOH , the carboxyl group is attached to a hydrogen atom. In other acids R stands for a carbon radical. Formic acid (boiling point 100.8°) is made by oxidizing formaldehyde. It is found in stinging nettles, and causes at least some of the irritation due to ant bites and bee stings.

Acetic acid. CH_3COOH melts at 16.7°C. and boils at 118°C. It is used in many chemical industries and is the acid component of vinegar. Through the agency of certain bacteria, a dilute solution of alcohol is oxidized by the air to acetic acid:



The bacteria that cause this change are present in the air in nearly all localities. It is due to the activity of these organisms that hard cider left in an open keg is soon changed to vinegar.

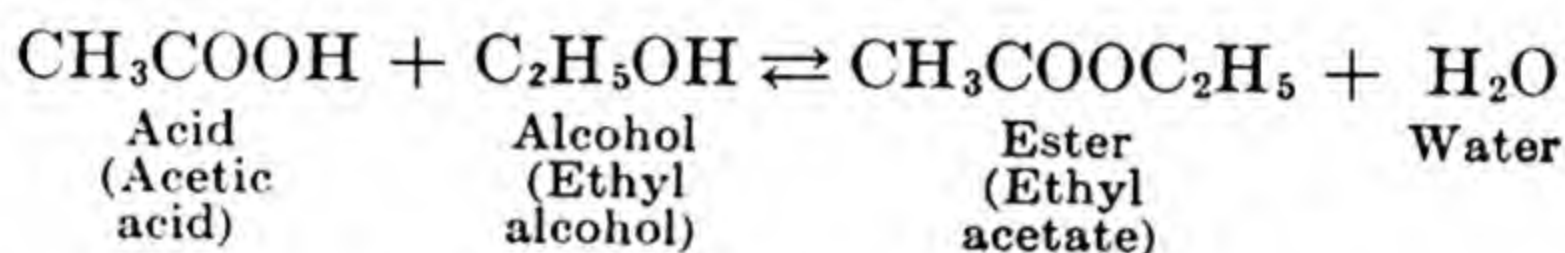
Other acids. Palmitic acid, $C_{15}H_{31}COOH$, and stearic acid, $C_{17}H_{35}COOH$, are waxlike solids. Oleic acid, $C_{17}H_{33}COOH$, is a colorless liquid. These acids are obtained from animal and vegetable fats and oils. When fats and oils are hydrolyzed, the principal products formed are palmitic acid, stearic acid, oleic acid, and glycerine.

PART 4

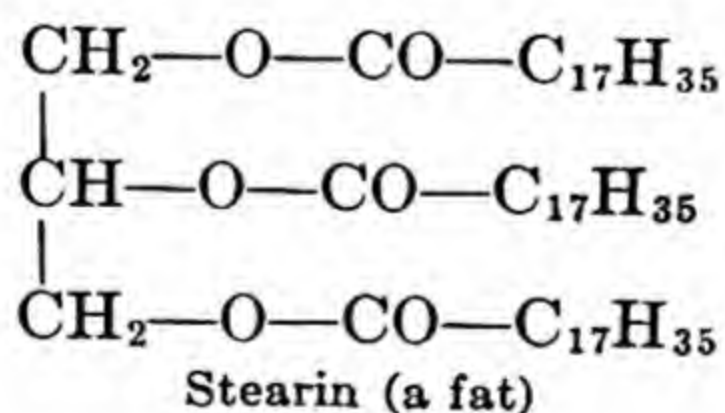
Esters and Ethers

Esters

An ester is formed when an alcohol and an acid combine, with the elimination of water. Ordinary alcohol reacts with acetic acid, forming an ester called *ethyl acetate*. The process is reversible, the ester being hydrolyzed when it is boiled with water containing a little acid or alkali:

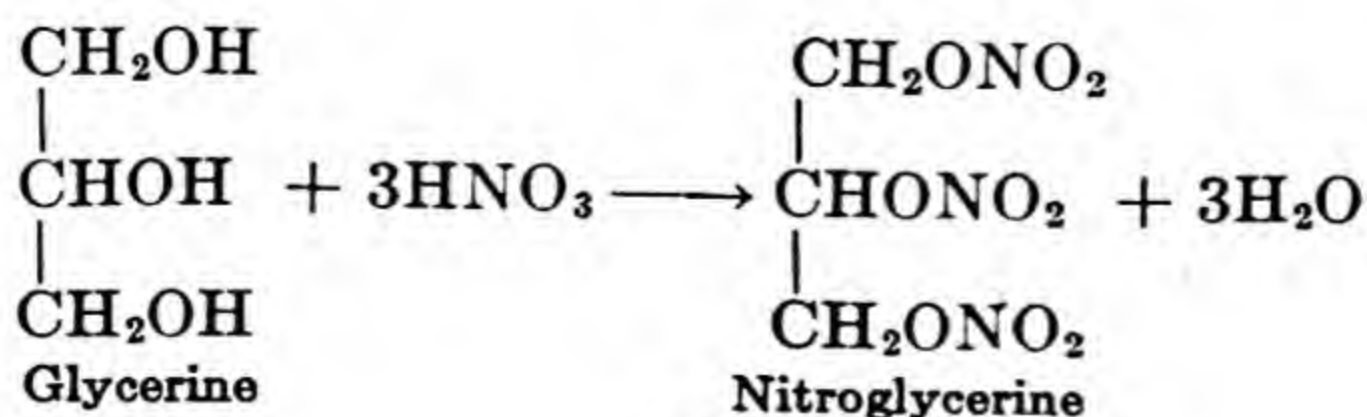


The esters made from acids and alcohols of low molecular weights are colorless liquids. They are characterized by agreeable odors, and many of them are used in synthetic flavors and perfumes. The natural animal and vegetable fats are mixtures of esters in which the alcohol called glycerine is combined with acids of high molecular weight. Stearin, a fat constituting the major part of beef tallow, is a compound of glycerine and stearic acid. It has the formula:



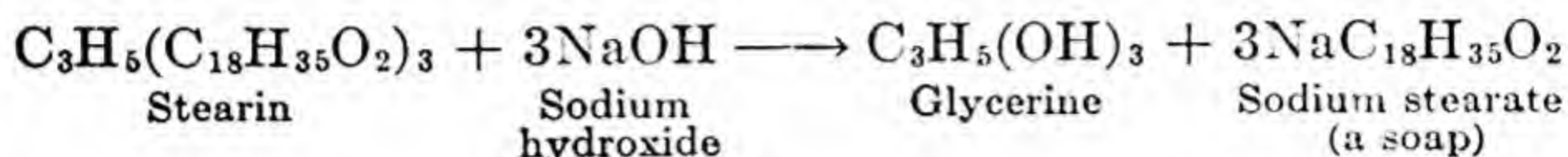
Palmitin and olein are fats in which esters of palmitic and oleic acids, respectively, are the main components.

Nitroglycerine is an ester. It is formed when nitric acid acts upon glycerine:



Nitroglycerine is a colorless liquid. It is insoluble in water but soluble in alcohol. It explodes when subjected to a sudden shock or when heated to a temperature of 250°C . Dynamite is made by saturating wood pulp with nitroglycerine.

Soaps. When a fat is boiled with sodium or potassium hydroxide, it combines with the base, forming a soap and glycerine:



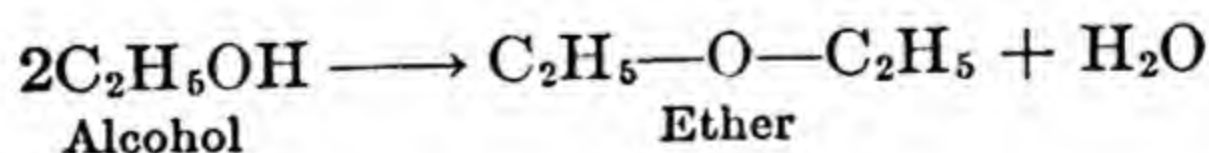
Sodium hydroxide produces a hard soap. Potassium hydroxide forms a soft soap. Salts of stearic acid, palmitic acid, and other acids of high molecular weights are called *soaps*.

Complex organic amines (derivatives of ammonia) are used instead of sodium hydroxide for the production of many soaps, shaving creams, and shampoos. When an ordinary soap is dissolved in water, it hydrolyzes, producing a small amount of free alkali. This alkali is often harmful to tender skins. The use of organic bases removes this danger.

There are good detergents which are not soaps. Some of these are as effective in hard water as in soft water. Sulfuric acid esters derived from alcohols of high molecular weight are used in the preparation of some of these compounds. The sodium salts of these acid esters are excellent detergents. One compound of this type has the formula $\text{C}_{17}\text{H}_{35}\text{CH}_2\text{OSO}_3\text{Na}$. Cleansing agents of this general type are sold under various trade names.

Ethers

The ethers are represented by the general formula $\text{R}-\text{O}-\text{R}$. The first two members of this series of compounds are gases. They are dimethyl ether, $\text{CH}_3-\text{O}-\text{CH}_3$, and methyl ethyl ether, $\text{CH}_3-\text{O}-\text{C}_2\text{H}_5$. By far the most valuable member of the series is the diethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$, commonly used as an anesthetic. It is made from ordinary ethyl alcohol by heating the alcohol with sulfuric acid:



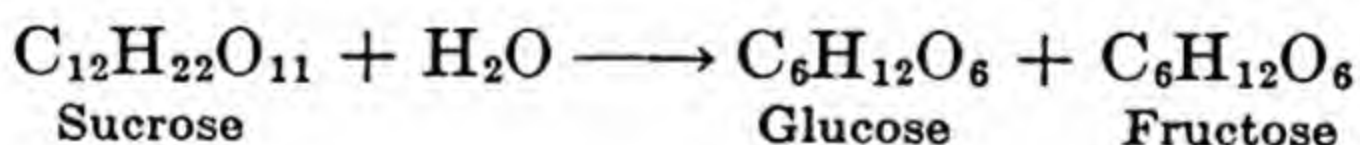
Ether is a light, colorless liquid with a characteristic odor. It is very volatile (boiling point 34.6°) and the vapor forms an explosive mixture with air. It is a good solvent for many types of organic compounds. It is practically insoluble in water but dissolves in all proportions in alcohol, gasoline, and benzene.

PART 5

Carbohydrates

Sugars and starches are the best-known representatives of a class of compounds called *carbohydrates*. They are composed of carbon, hydrogen, and oxygen, and in nearly all of them the hydrogen and oxygen are present in the same ratio as in water. When these compounds are decomposed by heat, the main products are water and carbon. The sugars are soluble in water and have a sweet taste, while the starches are insoluble in water and are tasteless. Wood, paper, and the solid portions of the stems and leaves of all plants are composed principally of cellulose which is classified as a carbohydrate.

Sucrose. The chemical name for ordinary sugar is sucrose. It has the formula $C_{12}H_{22}O_{11}$. We obtain it from sugar cane and from sugar beets. The annual consumption of sugar in the United States amounts to approximately 90 lb. for every man, woman, and child. When warmed with a dilute acid, sucrose is hydrolyzed (combines with water), and two simpler sugars are formed:



Glucose and fructose. As shown by the equation above, glucose and fructose have the same empirical formula, $C_6H_{12}O_6$. They have different structural formulas, however, and different chemical properties. Both are sweet, soluble sugars. Glucose, known also as dextrose or grape sugar, is used extensively in jellies, jams, and candies; and as an intermediate product, it is used in the manufacture of alcohol and acetic acid. Glucose is produced in large quantities by hydrolyzing starch which, in turn, is obtained from wheat, corn, rice, or potatoes. Fructose occurs in the free state (but mixed with glucose) in honey. In chemical combination with glucose it is present in cane sugar.

Starch. The composition of starch is accurately represented by the simple formula $C_6H_{10}O_5$, but its molecular weight is unknown. We have evidence that the molecule is very much heavier than that indicated by this simple formula, and we write the formula

$(C_6H_{10}O_5)_n$, in which n stands for an unknown number. Starch consists of very small granules, and the granules derived from different kinds of starch can be distinguished by examining them under a microscope. Corn and potatoes are the principal commercial sources of starch, but large quantities are prepared also from rice and arrowroot. Starch is one of our best foods.

Cellulose. The woody fibers of trees and the stalks and stems of all plants are composed principally of cellulose, $(C_6H_{10}O_5)_n$. Cotton, linen, and paper are composed of cellulose. Cellulose is not rendered digestible by cooking, and in this respect it differs from starch, which has the same chemical composition.

Compounds of cellulose have great commercial value. Cellulose derivatives are used in the manufacture of rayon fibers and in smokeless powder. Collodion is a solution of nitrocellulose in a mixture of alcohol and ether. Guncotton is a form of cellulose nitrate. When cellulose nitrate and camphor are dissolved together in a little alcohol, a solid substance called celluloid is formed. Cellulose nitrate is used also with camphor in the production of photographic films. Artificial leather is made by coating canvas with a solution of nitrated cotton. Pyroxylin is one of the many products that can be made by treating cotton with nitric acid.

Rayon. This valuable artificial textile is manufactured from cotton or from wood pulp. The first step in the process is treatment of the cotton with sodium hydroxide. This treatment forms soda-cellulose, a compound which reacts with carbon disulfide forming an orange-colored viscous liquid called *viscose*. The viscose is forced through platinum nozzles into a bath of sulfuric acid. In this way extremely fine threads are formed, which may be spun and woven to make cloth called *rayon*. The finished product has the same composition as cellulose. The rayon industry has grown tremendously in recent years. We use many times as much rayon as silk.

If the viscose is spread into thin sheets instead of being formed into threads, *cellophane* is formed. This finds extensive use in the wrapping of foods and various other articles.

Questions and Exercises

1. Chloroform has the formula $CHCl_3$. Calculate the per cent of hydrogen in this compound.
2. How is alcohol made from starch?
3. Outline two methods by which methanol is produced.
4. What is the chief commercial source of glycerine?

5. How is nitroglycerine made?
6. What is (a) an alcohol, (b) an ether, (c) an ester, (d) an acid, (e) a carbohydrate, (f) a hydrocarbon, (g) an aldehyde?
7. How are esters made?
8. What is (a) soap, (b) methanol, (c) celluloid?
9. How could you distinguish pure methanol from pure ethyl alcohol?
10. Equal weights of ethyl alcohol and acetic acid were mixed in making ethyl acetate. Which reagent was present in excess?
11. Give two methods for preparing glycerine from fats.
12. How much glycerine is required to make 500 lb. of nitroglycerine?
13. Ether vapor and air form an explosive mixture. Write an equation representing the oxidation of ether to carbon dioxide and water.
14. Write a structural formula for (a) alcohol, (b) ether, (c) acetic acid, (d) chloroform, (e) carbon tetrachloride.
15. What is (a) a carbohydrate, (b) dynamite, (c) a fat, (d) starch, (e) sucrose, (f) glycol, (g) rayon?

PART 6

Fuels

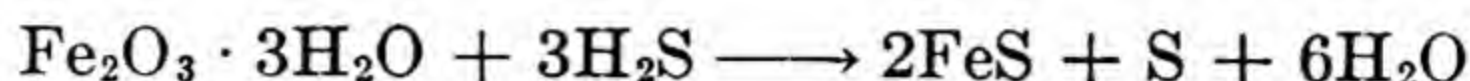
One of the greatest contributions of industrial chemistry to the world has been the production of gaseous and liquid fuels. Coal and wood, which have long been used as fuel, are not easily handled and they are expensive and difficult to transport. A coal or wood furnace has to be continually replenished, and this means the exertion of physical energy. Gas and liquid fuels, on the other hand, are easy to transport through pipes. Burners utilizing these fuels can be made to burn automatically, so that there is a continuous production of heat without need of much supervision. Such fuels are rapidly replacing the solid type in our homes, factories, and vehicles.

Gaseous fuels. *Natural gas* is found in many parts of the world, often being associated with petroleum. It is obtained by drilling into the earth and establishing wells where the deposits occur. The gas consists chiefly of the hydrocarbons having low molecular weights, such as methane, ethane, propane, and butane. It usually contains some nitrogen, and sometimes carbon dioxide and helium. The gas wells of Kansas, Oklahoma, and Texas contain helium.

Coal gas. In regions where deposits of coal are found, it has been customary for many years to produce a gaseous fuel known as coal gas. When soft coal, such as bituminous coal, is heated in the absence of air (destructive distillation), large volumes of gas are driven off. This gas is composed largely of methane and hydrogen, which are both combustible gases that burn with the liberation of large quantities of heat. The gas also contains appreciable amounts of ammonia and hydrogen sulfide. A liquid product, coal tar, and a solid residue of coke are other products of the distillation of coal. From the coal tar we obtain benzene, toluene, naphthalene, and anthracene, all valuable members of the aromatic series of hydrocarbons.

Ammonia is removed from the coal gas by spraying the gas mixture with water or dilute acid in compartments called "scrubbers." This process is one of our main sources of ammonia.

Hydrogen sulfide is removed by passing the gas over moist ferric oxide:



When the gas has been purified in this manner, it is stored in huge gas holders, from which it is distributed to the consumer.

Water gas. The use of water gas has replaced that of coal gas to a great extent. Water gas is made by passing steam through a mass of heated coke or anthracite coal. The reaction that takes place may be represented by the following equation:

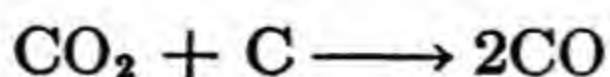


Water gas, then, is largely a mixture of hydrogen and carbon monoxide.

The process is carried out by first igniting a part of the coal or coke, and then blowing a blast of air through it. This blast heats the coal to a bright, glowing temperature. The air is then shut off, and blasts of steam are sent through the hot coal. The hydrogen and carbon monoxide formed are then removed. When the coal becomes cooled, the steam is shut off, and air is again blown through until the carbon becomes very hot. This process of alternately blowing air and steam through the coal continues until the coal is used up. The cost of producing water gas is considerably below that of producing coal gas.

Since hydrogen and carbon monoxide both burn with a non-luminous blue flame, other substances must be added if the gas is to be used for illuminating purposes. For this purpose a hydrocarbon oil is sprayed into the gas. The mixture is then heated to a high temperature, which "cracks" the larger liquid hydrocarbon molecules into smaller gaseous particles. When the gas burns, these molecules liberate free particles of carbon which become heated to a white heat, giving out light. Water gas, besides being useful as a fuel, is finding extensive use as a source of hydrogen. It is also being used as fuel in airships. Since carbon monoxide is highly poisonous, water gas is more dangerous to use than either natural gas or coal gas.

Producer gas. An important industrial fuel called producer gas is made by blowing air through a bed of coal five or six feet deep. The coal is arranged so that the lower layers are red-hot and the upper layers are much cooler. The coal burns to carbon dioxide at the bottom of the pile, but as the carbon dioxide rises through the pile of hot carbon, it is largely reduced to carbon monoxide:



Producer gas contains, in addition to carbon monoxide, all of the nitrogen from the air which was blown into the furnace. This makes up nearly half its volume; hence producer gas has a low heating value. In some cases a "semiwater gas" is made by blowing some steam with the air through the fuel bed. The gas then contains some hydrogen mixed with the carbon monoxide and nitrogen.

Producer gas is obtained as a by-product in blast-furnace operations. The gas is caught at the outlet of the furnace and used as a source of heat under the furnace.

Liquid fuels. The principal liquid fuels are ethyl alcohol, methyl alcohol, and petroleum products.

The alcohols are too expensive for use as fuel on a large scale. They are used extensively, however, for small stoves and heaters. They burn with a hot, clean flame.

Petroleum is the source of most liquid fuels. These include gasoline, kerosene, and the oils containing larger hydrocarbon molecules which are used as fuel in furnaces, locomotives, and boilers.

Questions and Exercises

1. Name four gaseous fuels, and give the composition of each.
2. How many liters of water gas, measured at standard conditions, can be formed by the action of an excess of steam on 1000 kg. of carbon?
3. How many liters of air would be required to burn completely 1000 liters of water gas? Consider that all gases are measured under standard conditions.
4. What is the composition of natural gas?
5. Why is it safer in the home to burn natural gas than to burn water gas?
6. Why is coal tar removed from coal gas before it is sold to the consumer?
7. Why is the hydrogen sulfide present in coal gas removed?
8. Why are gaseous and liquid fuels more convenient to use than solid fuels?
9. What is meant by the term "destructive distillation"?
10. Why are oils heavier than gasoline better to use in furnaces, and under boilers?
11. Why is gasoline instead of kerosene or crude oil used in automobile engines?
12. What are the products of the combustion of gasoline in an excess of air?
13. What is formed when gasoline burns in an automobile engine? Explain

UNIT XXI

Plant and Animal Life

PART 1

Elements Essential to Plant Life

Thirteen elements are known to be indispensable to plant growth. These elements are oxygen, hydrogen, carbon, nitrogen, phosphorus, potassium, sulfur, calcium, magnesium, iron, manganese, zinc, and boron. Of these elements, oxygen and hydrogen are supplied in the form of water; and carbon, in the form of carbon dioxide. Uncombined oxygen is obtained from the atmosphere. Some plants are able to utilize atmospheric nitrogen, but most plants derive their nitrogen from nitrates in the soil.

The principal reactions occurring in green plants are the syntheses of sugars, starches, celluloses, and proteins from water, salts, and carbon dioxide. These transformations occur in the leaves and stems of plants under the influence of light, and they are called *photochemical processes*. Energy is required to convert water, carbon dioxide, and salts into the compounds found in plants, and the energy necessary for these transformations is derived from the sun.

Chlorophyll, the green coloring matter in the leaves, plays an important part in the production of carbohydrates by plants. Light alone will not change pure carbon dioxide and water to starch, but in the presence of certain catalysts this change is accomplished, and chlorophyll is an effective catalyst for the reaction.

Many types of compounds are produced by plants. Nitrogen and phosphorus constitute a part of every cell in every living plant. In many different kinds of molecules the elements potassium, phosphorus, oxygen, nitrogen, sulfur, calcium, magnesium, and iron are woven into the complex structures of the compounds that constitute leaves, stems, roots, and seeds. The extraction of these elements from the soil by successive crops often leaves the soil deficient in some of them. Potassium, phosphorus, and nitrogen are the elements usually taken out of the soil in larger quantities than they can be supplied by natural processes. To correct the

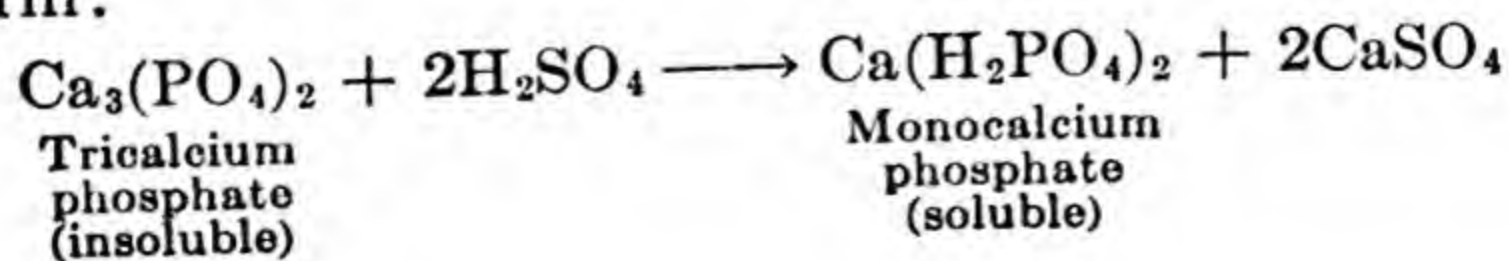
deficiency, these elements are added to the soil in the forms of various substances called *fertilizers*.

As far back as written history goes, it has been recognized that manures are beneficial to growing crops. Manure from any source contains phosphorus, potassium, and nitrogen in the form of soluble compounds. The decay of dead vegetable and animal matter brought about by bacterial action is another means of returning to the soil necessary elements and compounds. Some of the nitrogen in such organic matter is released as free nitrogen gas, and some of it is converted into ammonia. Certain bacteria are able to oxidize ammonia to nitrites (salts of nitrous acid) and other micro-organisms convert nitrites into nitrates (salts of nitric acid). In nitrates the nitrogen is once more in a form that plants can use.

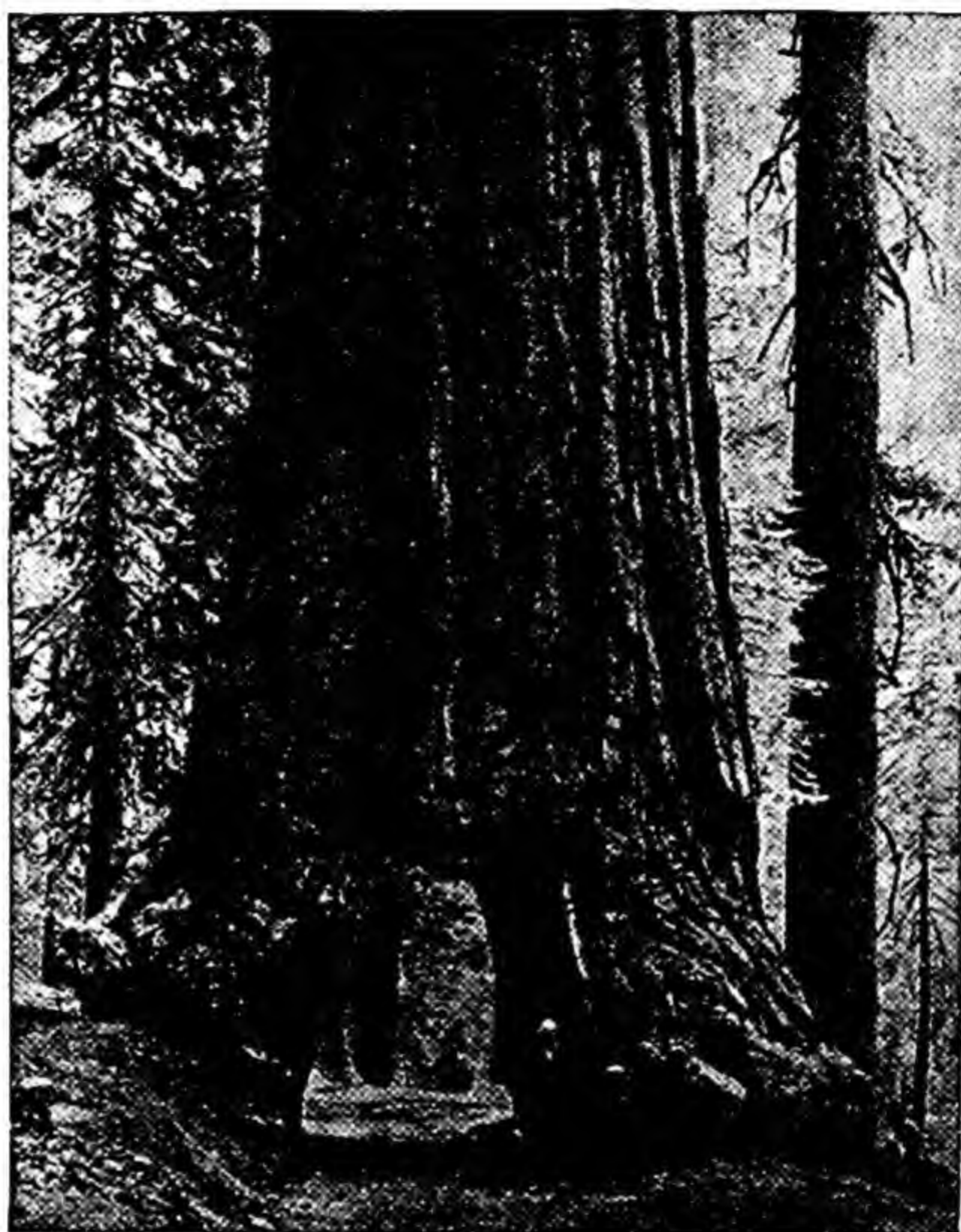
Fortunately there are a few species of bacteria that are able to convert free atmospheric nitrogen into nitrogen compounds. The process of making nitrogen gas unite with other elements to form compounds is called *nitrogen fixation*, and the nitrogen contained in such compounds is called *fixed nitrogen*. Among the most valuable of the bacteria in the soil are the nitrogen-fixing bacteria that live on the roots of alfalfa, clover, peas, and other legumes. These organisms derive part of their food supply from the starchy substances in the roots of the plants, but at the same time they take nitrogen from the air and convert it into forms that the plant can use. This fixation makes it possible to grow legumes in a soil that contains relatively little nitrogen. If, then, the crop is plowed under, or allowed to decay on the soil, the fixed nitrogen contained in the plants goes into the soil and is soon converted into salts that can be used by any crop.

Other natural sources of fixed nitrogen are the Chile nitrate beds and coal. (See destructive distillation of coal, page 292.) The nitrate beds in Chile cover an area 200 miles long and from two to five miles wide, to an average depth of about five feet. It is believed that the nitrate beds originated in vast deposits of guano (bird manure). Bacteria caused the nitrogen in this organic matter to be oxidized to the nitrate form. The artificial methods that have been devised to convert free nitrogen into compounds have been described (see pages 254 and 256).

In the United States alone, more than 3,500,000 tons of phosphate rock are converted into phosphate fertilizers annually. The crushed rock is treated with sulfuric acid to convert it into a soluble form:



Potassium is added to the soil for fertilizer purposes in the form of potassium chloride. We were formerly dependent upon the Stassfurt mines in Germany for our supply of potassium salts, but large deposits of potash have been located in this country and they are being developed rapidly. The best local sources at the present time are the Carlsbad deposits in New Mexico and Searles Lake in California.



Courtesy, National Park Service

Fig. 174. The Wawona Tree, Yosemite National Park. An automobile road runs through the trunk of the living tree.

Manganese, boron, and zinc are needed in minute quantities only. It is probable that these elements act as catalysts to help the plant take up the other necessary elements. Further research is required to disclose the manner in which these elements are used.

The capacity of a plant to assimilate (use for cell production) carbon dioxide, water, and compounds derived from the soil depends largely upon climatic conditions. Temperature and rainfall are among the most important factors. Some plants are very susceptible to diseases, and others successfully resist disease and survive unfavorable climatic conditions. One variety of wheat is ruined by rust, and another kind of wheat growing in the same field contains compounds that protect it from the rust fungi.

Slight differences in chemical composition determine which shall live and which shall die when plants are subjected to unfavorable conditions. The Sequoia trees of California are especially resistant to plant disease, and their thick bark, which does not burn readily, enables them to survive forest fires. Many of these grand monarchs of the forests are more than 20 ft. in diameter and 300 ft. high. Some of them have attained an age of 4000 years.

Questions and Exercises

1. Name six elements that are essential to plant life.
2. Name the three elements that are used in greatest quantities by plants.
3. What is the source of the carbon found in starch and cellulose?
4. Why does the production of a crop reduce the fertility of the soil?
5. Name three elements that are sometimes added to the soil to increase its fertility.
6. Describe two processes of nitrogen fixation as accomplished by bacteria.
7. Describe two industrial processes for nitrogen fixation.
8. How does sunshine aid in the growth of plants?
9. What weight of phosphorus is contained in 1 ton of tricalcium phosphate?
10. What weight of sulfuric acid is required to convert 1 ton of phosphate rock into a soluble form?
11. Find the weight of nitrogen in 500 lb. of calcium nitrate, $\text{Ca}(\text{NO}_3)_2$.
12. How much nitric acid is required to make 500 lb. of calcium nitrate from calcium carbonate and nitric acid?

PART 2

Compounds Essential to Animal Life

Chemistry has rendered an important service to mankind in placing the problems of nutrition on a scientific basis. We know the kinds and the quantities of foods that must be consumed to support the normal processes of life. Certain foods have special duties to perform, and a varied diet is required to supply all the necessary types of compounds. Our corn crop alone would furnish calories enough for the entire population of the country, but corn lacks some essential substances and has an excess of others. We would soon become undernourished and ill if we tried to live on corn alone.

The first function of food is to provide energy for our activities. Our foods undergo chemical reactions that release within the system sufficient heat to keep the body warm, and sufficient chemical energy to provide for muscular activity—that is, to enable us to work and play.

The second function of food is to repair the tissues of the body as rapidly as they wear out and, if the body is still growing, to provide additional tissue cells. An exchange of chemical materials is going on all the time between the blood and the living cells in the body. The blood receives from the intestinal tract a supply of new material in the form of digested food. This building material is delivered by the blood stream to the cells of every tissue, and from each cell the blood carries away the waste products of metabolism, discharging these waste products from the system principally through the lungs and the kidneys.

The principal classes of foods required by man are (1) carbohydrates, (2) fats, (3) proteins, (4) vitamins, (5) inorganic salts, (6) water. The last three classes of compounds do not supply energy, but they are essential components of the diet.

The respiration calorimeter. The first successful method for measuring the exact amount of energy required by the body under varying conditions of activity was devised by W. O. Atwater and F. G. Benedict. They built a calorimeter in which a man could live for several days at a time. It was a room 7 feet long, 4 feet

wide, and 6 feet high, with walls, ceiling, and floor built like a refrigerator so that heat could not pass through. This insulated box or room contained a cot on which a man could sleep and a stationary bicycle upon which he could exercise. The room was airtight except for an inlet to admit a measured flow of air and an exit tube through which the air could be drawn out. The temperature of the entering air was carefully controlled, and the carbon dioxide and water vapor in the air supplied and in the air withdrawn were measured. The room was equipped with the finest known electrical devices for measuring temperature changes, the temperature being indicated on instruments in the laboratory outside the box. The temperature control was so accurate that if the man in the calorimeter should get up from the cot, the energy involved in the action was recorded by the instruments. The food consumed by the man in the calorimeter was weighed, and the heat evolved by burning an exactly equivalent quantity of the same kind of food was measured. The undigested waste products likewise were weighed and burned, and the heat released by these unused residues was measured.

These experiments led to the discovery that the energy derived from carbohydrates in life processes is exactly equivalent to the energy that could be derived from the same materials by burning them in a furnace. The energy derived from proteins in life processes is not quite equal to the heat released when they are burned in the air, for the oxidation products obtained in the two cases are not identical. The respiration calorimeter made it possible to determine just how much carbon dioxide is exhaled and how much heat is radiated from the body in any specified time by an individual at rest or at work.

With a knowledge of the energy requirements of the system in various conditions of activity, and a knowledge also of the calorific value of foods, we can calculate the quantities of foods necessary to meet the average nutritional demands of the body.

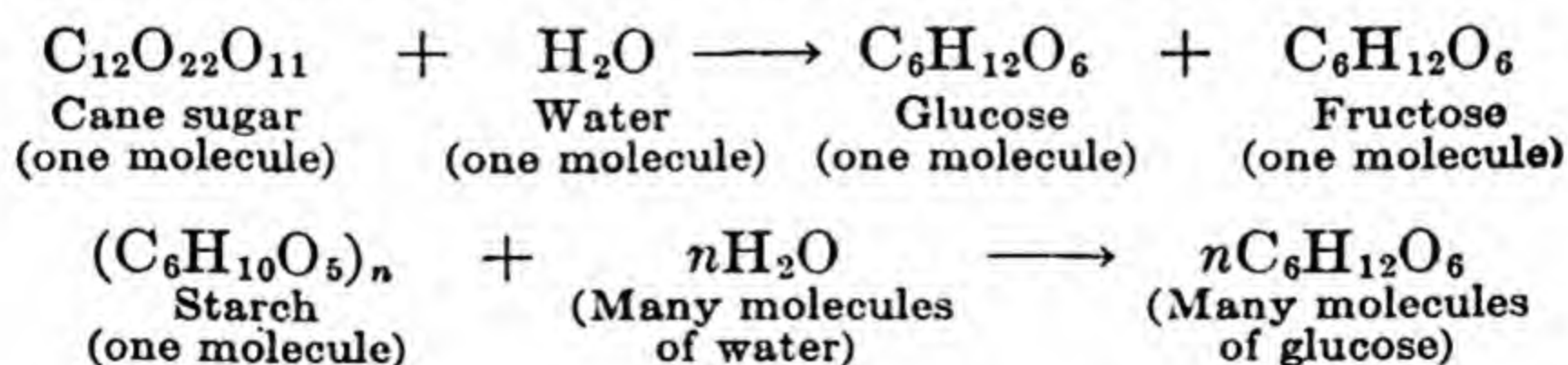
A child from two to six years old requires about 40,000 calories (40 kilogram-calories) of energy per day for each pound of body weight, or a total of 1000 to 1500 kg.-cal. per day.* From six to twelve years of age the normal requirement is about 34 kg.-cal. daily for each pound of body weight.

Carbohydrates. The sugars and starches belong to the class of compounds known as carbohydrates. They constitute our

* A kilogram-calorie (Cal. or kg.-cal.) is the quantity of heat required to raise the temperature of 1000 g. of water 1°C. It is sometimes called a large calorie. A small calorie (cal.) is the quantity of heat required to raise the temperature of 1 g. of water 1°C.

principal sources of muscular energy and heat. Among the foods that supply large quantities of carbohydrates we have vegetables, cereals, and sugar. Sugar and starch are pure carbohydrates. Starch is the chief solid component of potatoes, wheat, and corn. The average energy value of carbohydrate food is 4 kg.-cal. per gram or 1818 kg.-cal. per pound. If sugar were less expensive we could use it as a fuel in our furnaces. Every pound of sugar burned to carbon dioxide and water would release 1818 kg.-cal. of heat, or enough heat to elevate the temperature of 400 lb. of water 10°C. When sugar is consumed in the diet it undergoes many changes in the course of metabolism, but ultimately it is converted into carbon dioxide and water; and in the process of changing 1 lb. of sugar to carbon dioxide and water in the living cells of the body 1818 kg.-cal. of heat are made available for use. Part of this energy appears as heat, which is used in keeping the blood at its normal temperature, and part of it is converted into muscular energy. The water and salts contained in foods are essential to life but they have no fuel value.

In the alimentary tract such foods as starch and cane sugar react with water, forming glucose and other simple sugars. The reaction of cane sugar or starch with water is called *hydrolysis*. Glucose, a sugar having the formula $C_6H_{12}O_6$, is formed from starch by hydrolysis. The digestion of starch consists of hydrolysis; that is, it is a process of adding water and splitting the complex starch molecules into simple sugar molecules. Cane sugar, $C_{12}H_{22}O_{11}$, reacts with water in the process of digestion, forming two simple sugars, each having the formula $C_6H_{12}O_6$. One of these sugars is glucose; the other is called fructose. The reactions for the digestion of sugar and starch may be written:



In the laboratory, starch can be converted into glucose by boiling it with dilute hydrochloric acid. Corn syrup is made in this way. In the body this change is brought about by chemical substances called *enzymes*.

Fats. Butter, olive oil, and lard are representatives of an important class of foods known as fats, the liquid members of this group of substances being commonly called oils. The fats and oils can be hydrolyzed by heating them with steam or by boiling them with acids or bases or by the action of enzymes. When fats

are decomposed by hydrolysis (addition of water), they yield glycerine and organic acids.

Nature has provided a means of storing fats in the tissue so that a reserve supply is available for emergencies. When the diet does not furnish an adequate quantity of fat, the system is able to synthesize fats from carbohydrates. Owing to this remarkable power of living cells, it is possible to fatten animals by feeding them grain, potatoes, and other foods that are composed principally of carbohydrates. The calorific value of a pure fat is 9 kg.-cal. per gram.

Proteins. The major part of the solid matter in muscle, skin, hair, nails, and all of the special organs of the body, including the heart and the lungs, is composed of compounds known as *proteins*. All proteins contain nitrogen combined with carbon, hydrogen, and oxygen, and many of them contain sulfur, phosphorus, and other elements in addition to nitrogen, carbon, hydrogen, and oxygen. It will be recalled that carbohydrates and fats contain carbon, hydrogen, and oxygen only. The carbohydrates and fats are our chief sources of energy, but they cannot take the place of proteins in building new tissues of the body or in repairing worn-out cells. No substitution can be made for proteins. Starvation would be the result of eliminating proteins from the diet even if all other kinds of foods were consumed in large quantities. Every living cell contains nitrogen and phosphorus. The plants are able to use inorganic sources of phosphorus and nitrogen in the synthesis of the proteins, but animals can utilize these elements only in the form of carbon compounds. We are dependent upon plants for the synthesis of these compounds. We may derive our protein supply directly from vegetables, fruits, and nuts, or from meat, but the proteins contained in meat were obtained from plants by the animals that supply our needs.

Eggs, cheese, fish, poultry, and all kinds of lean meat are rich in proteins. In less concentrated forms, part of the protein of our diets is derived from bread, cereals, and milk. The white of an egg (egg albumen) is a nearly pure protein substance. The yolk of an egg contains fats as well as proteins. The average calorific value of the proteins contained in foods is 4 kg.-cal. per gram.

The term *ash* refers to the residue of mineral matter which remains when a sample of the food is heated in air until no further decomposition can be effected by this means.

The energy value of a food may be determined experimentally by burning a weighed sample of the substance and measuring the heat evolved, or it may be calculated from the percentage composition of the food. Let us calculate the calorific value of rice.

AVERAGE COMPOSITION (PER CENT) AND FUEL VALUES OF SOME COMMON FOODS

Commodity	Water	Protein	Fat	Carbo- hydrate	Ash	Kg.-cal. per 100 grams
Apples.....	84.6	0.4	0.5	14.2	0.3	63
Asparagus.....	94.0	1.8	0.2	3.3	0.7	22
Beans (dried).....	12.6	22.5	1.8	59.6	3.5	345
Beef (lean).....	70.0	21.0	7.9	—	1.1	155
Beets.....	87.5	1.6	0.1	9.7	1.1	46
Bread (white).....	35.3	9.2	1.3	53.1	1.1	260
Butter.....	11.0	1.0	85.0	—	3.0	769
Cabbage.....	91.5	1.6	0.3	5.6	1.0	32
Carrots.....	88.2	1.1	0.4	9.3	1.0	45
Chicken.....	63.7	19.3	16.3	—	1.0	224
Eggs.....	73.7	14.8	10.5	—	1.0	154
Lettuce.....	94.7	1.2	0.3	2.0	0.9	16
Milk.....	87.0	3.3	4.0	5.0	0.7	69
Oatmeal.....	7.3	16.1	7.2	67.5	1.9	400
Olive oil.....	—	—	100.0	—	—	900
Oranges.....	86.9	0.8	0.2	11.6	0.5	51
Peanuts.....	9.2	25.8	38.6	24.4	2.0	548
Potatoes.....	78.3	2.2	0.1	18.4	1.0	83
Prunes (dried).....	22.3	2.1	—	73.3	2.3	302
Rice.....	12.3	8.0	0.3	79.0	0.4	351
Salmon.....	64.6	21.2	12.8	—	1.4	200
Spinach.....	92.3	2.1	0.3	3.2	2.1	24
Tomatoes.....	94.3	0.9	0.4	3.9	0.5	23
Wheat flour.....	11.9	13.3	1.5	72.7	0.6	359

The table indicates that dry rice is 79 per cent carbohydrate, 0.3 per cent fat, and 8 per cent protein. Using a 100-g. sample and applying the calorific values mentioned above, we have:

$$\begin{array}{r} 79 \times 4 = 316.0 \\ 0.3 \times 9 = 2.7 \\ 8.0 \times 4 = 32.0 \\ \hline 350.7 \end{array}$$

That is, rice supplies 350.7 kg.-cal. per 100 g. of rice or 3.507 kg.-cal. per gram of rice. Samples of rice and of other foods derived from different sources vary a little in composition and the decimal part of this value is meaningless. We may accept the value of 3.5 kg.-cal. per gram as accurate enough for our purpose. A pound is equal to 453.6 g. To determine the energy value of 1 lb. of rice, we have

$$453.6 \times 3.5 = 1,587 \text{ kg.-cal. per pound}$$

or 158,700 small calories per pound.

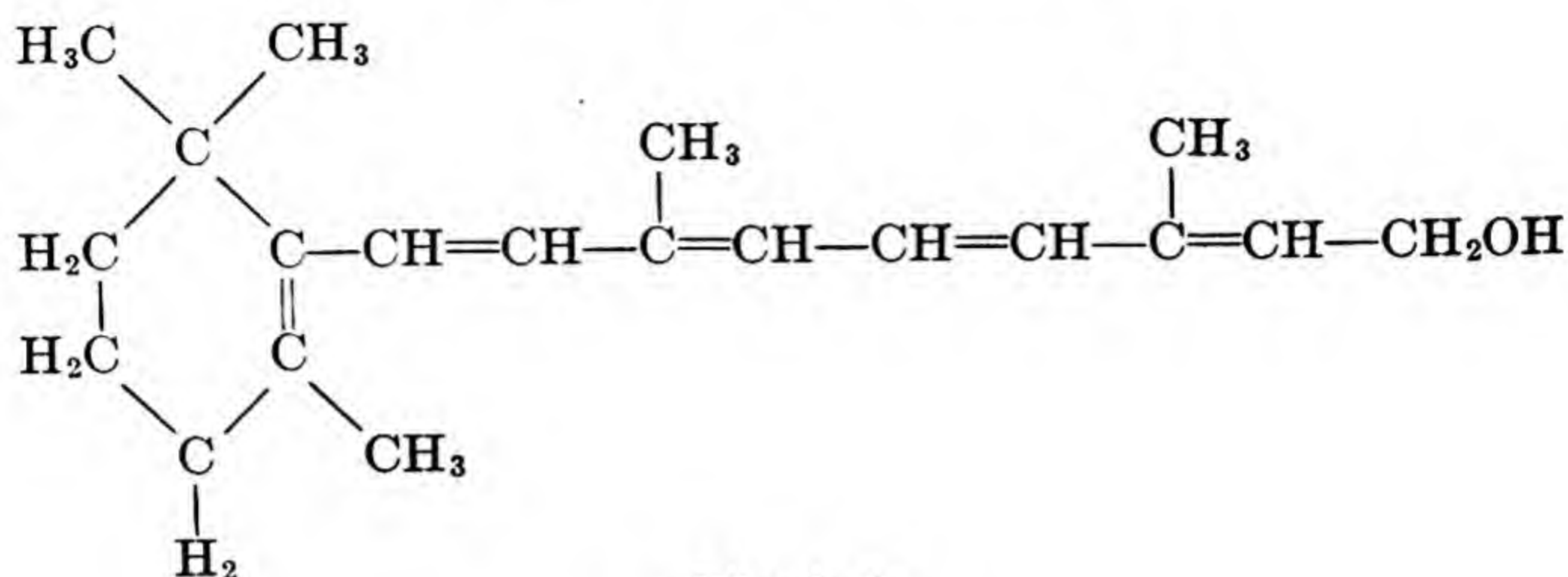
All the energy that we expend at work and at play must be derived from our food. Even when we are sleeping, chemical changes are going on, though at slower rates. The total energy required per day to sustain our activities has been determined by measuring the quantity of carbon dioxide exhaled per hour and by measuring the amount of heat radiated per hour under varying conditions of exercise. The energy requirement varies greatly with the kind of work that must be done. For an adult man the *average* daily requirement is about 3000 kg.-cal. In proportion to body weight, a growing child needs much more food than does an adult.

Vitamins. The elements required for the nutrition of man are found in the carbohydrates, fats, and proteins, water and salts, but the normal processes of nutrition cannot occur without the aid of traces of some other substances. Certain compounds which are required in extremely small quantities to regulate the chemical reactions occurring in living cells are called *vitamins*. The functions of vitamins in living tissue have been likened to the functions of spark plugs in an automobile engine. The fuel required to operate the motor is present in the form of gasoline and air. The energy derived from the spark is negligible; nevertheless, the spark is just as necessary as the gasoline. An abundance of food meets our nutritional requirements only when certain vitamins are present to promote the chemical changes involved in life processes.

Vitamin A. A substance present in eggs, butter, milk, cheese, liver, carrots, apricots, spinach, parsley, and many other foods is known as vitamin A. It is related to the yellow compound carotene, found in many fruits and vegetables. It is essential to growth and good health. An animal, fed on a diet lacking vitamin A but containing an abundance of everything else, ceases to grow, gradually loses weight, and finally becomes ill and dies.

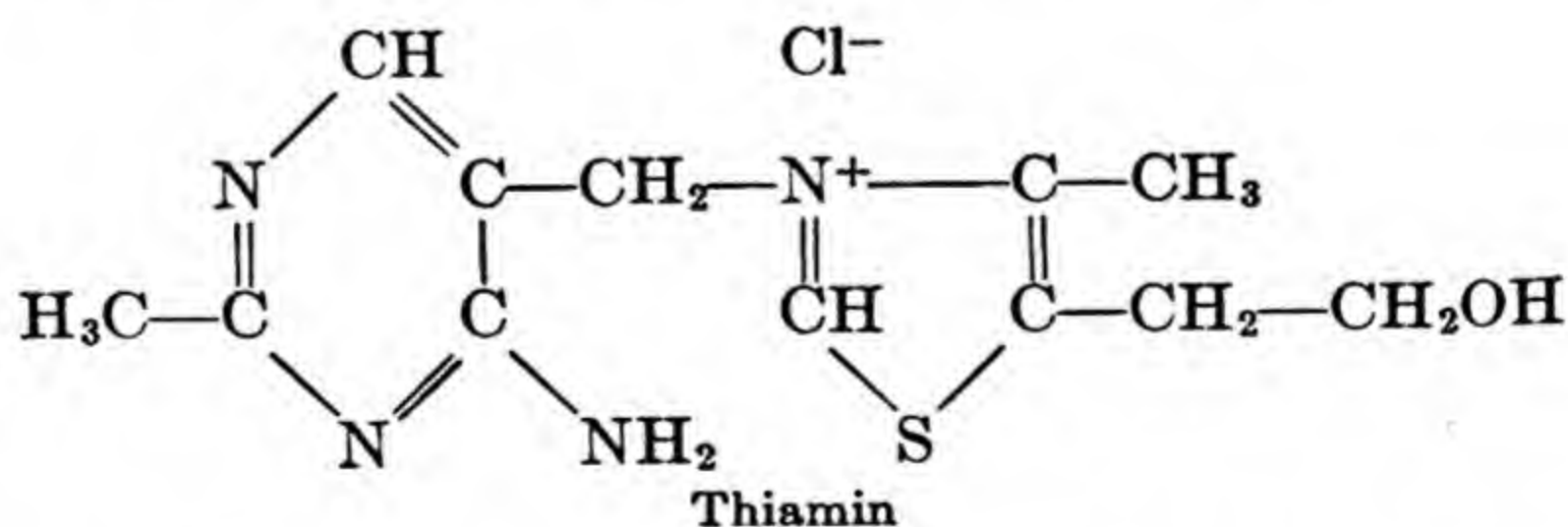
One of the first symptoms of the lack of vitamin A, in man, is subnormal vision in dim light. Ability to see in the dark is dependent upon the presence in the eye of a pigment called *visual purple*. This substance is destroyed by exposure to bright light, and it develops again in the dark. The rate of development of visual purple, up to a certain maximum, is proportional to the amount of vitamin A delivered to the eye by the blood stream. Many individuals experience difficulty in driving at night. The glare of an approaching headlight destroys the visual purple in the eyes and, due to vitamin-A deficiency, the restoration of the pigment is retarded. For a short time after encountering a glaring light the driver is blind.

Vitamin A has the formula $C_{20}H_{30}O$. The atoms are arranged as shown in the following structural formula.*



Vitamin A

Vitamin B. A nerve disease known as *beriberi* has prevailed in the Orient for many centuries. Prior to the beginning of the twentieth century it was not uncommon to find 10 per cent of the men in the Chinese and Japanese armies and navies afflicted with this disorder. The origin of the disease was traced to the diet of the enlisted men. Polished rice was used by all as the chief food. The disease could be cured by using whole rice instead of the milled product. Rice bran contains *vitamin B*. Rice flour lacks this essential group of substances. Several vitamins occur together in rice bran; the mixture is called "vitamin-B complex." The best known member of the complex is thiamin or vitamin B_1 . It was isolated in crystalline form from rice bran and from yeast as early as 1926 and ten years later it was synthesized.†

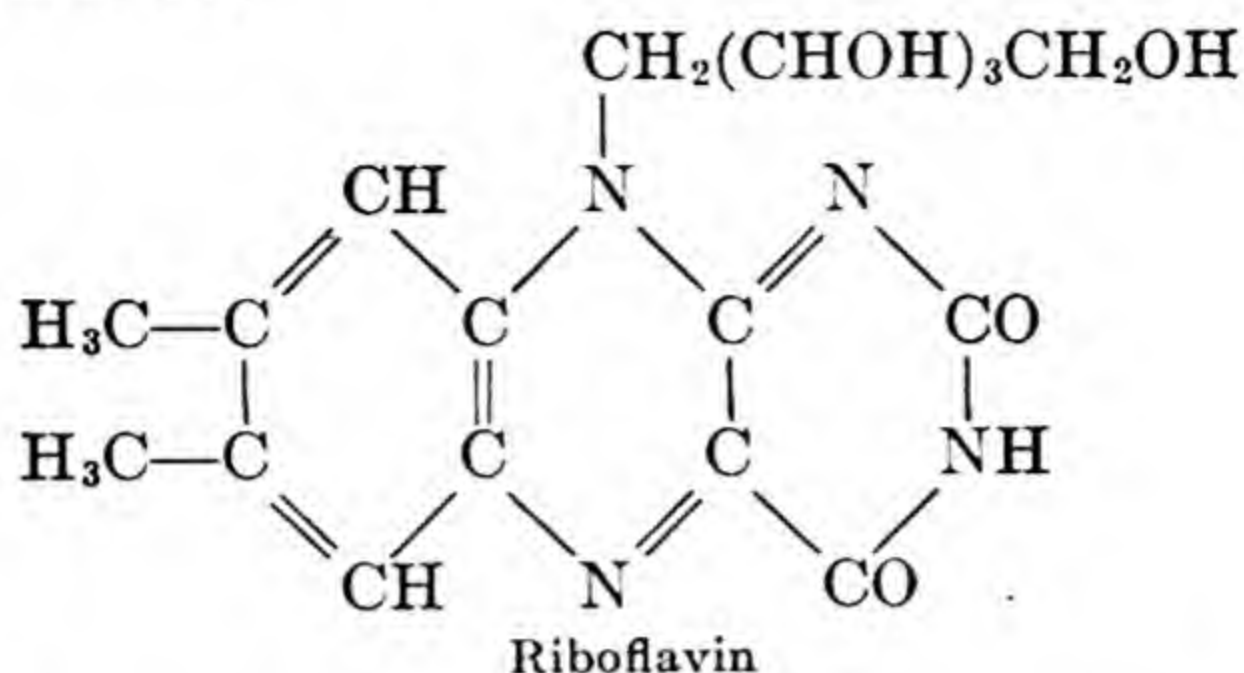


Among the best sources of this vitamin in ordinary foods are the bran and germ of cereals. It is found also in liver, beans, peas, and peanut butter. The compound is present in small amounts in almost all kinds of foods.

* The structural arrangements of atoms in molecules containing carbon are determined by methods explained in organic chemistry.

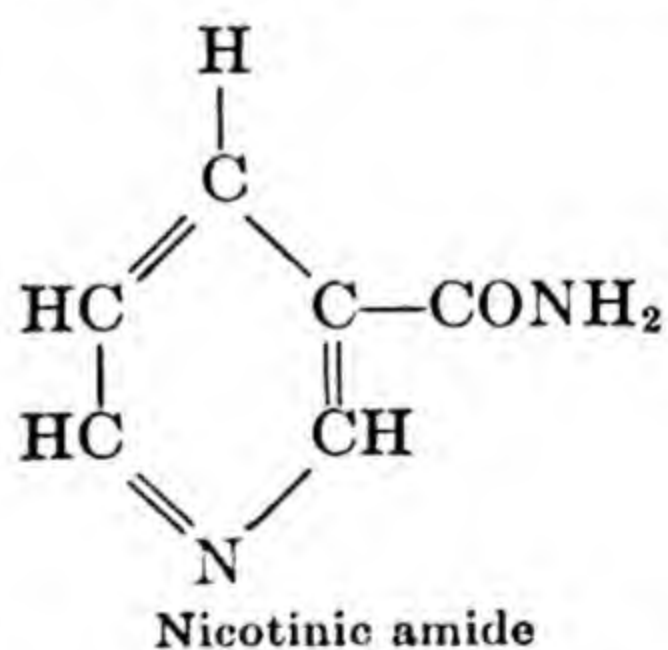
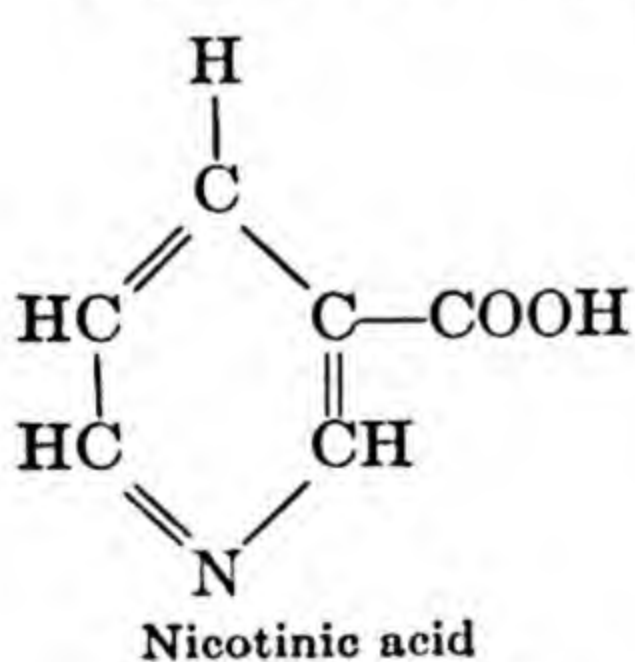
† R. R. Williams and J. K. Cline, *J. Am. Chem. Soc.* **58**, 1504 (1936).

Vitamin B₂ (riboflavin) has been isolated from many natural sources and it has been prepared synthetically. It corresponds to the following formula:



A disease of the eye develops in animals when a diet which is free from this substance is used; and well-developed cases have been cured by addition of the compound to the diet. Some skin disorders also seem to be due to insufficient riboflavin in the food. Riboflavin is a growth-promoting substance. Young animals fail to attain normal size if deprived of this factor of the vitamin-B complex.

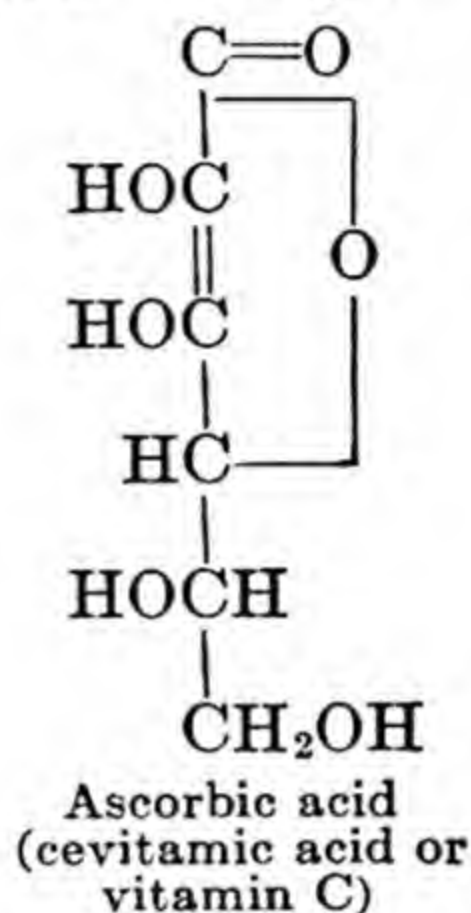
Another component of the vitamin-B complex, nicotinic acid, protects us from the disease known as pellagra. The amide of nicotinic acid is apparently equally efficient, and both of these compounds are present in many plant and animal foods.



Nicotinic acid and its derivatives are detrimental to health if taken in large doses. There is no danger of an overdose from natural food sources, but too much of the synthetic product could be added to the diet.

Vitamin C. A disease known as scurvy is prevalent wherever it is difficult to obtain green foods. It is due to lack of vitamin C in the diet. This vitamin is abundant in grapefruit, oranges, lemons, lettuce, green peas, spinach, and tomatoes. Scurvy should disappear from the list of human ills for its cause is fully understood and the remedy is inexpensive. From ancient times down to the twentieth century scurvy was common among

seamen and others who, for long periods, were deprived of fruits and fresh vegetables. Early in the seventeenth century the crew on a British ship made a voyage of four months duration without the development of a single case of scurvy. They had lemons, or as they called them, "limes," in their supply of foods. As a result of this experience, and later confirmation of the efficacy of lemon juice, the British Parliament required the use of lemon juice as a regular addition to the diet on all ships in the Navy. British sailors are still called "limeys."



Vitamin C has been identified as ascorbic acid which is relatively plentiful in lemons. It is now available in pure crystalline form.

Vitamin D. A compound known as vitamin D is responsible for the proper assimilation of calcium and phosphorus in the bones. Rickets is a disease of the bones caused by a deficiency of vitamin D in the diet. Cod-liver oil which has been exposed to ultraviolet light has been used with success in the treatment of rickets. Cod-liver oil contains a substance, called *ergosterol*, which is changed to vitamin D by the action of light. The vitamin is present to some extent in all untreated fish-liver oils, but the quantity of the vitamin is increased in each case by exposure to ultraviolet light. Egg-yolk, milk, butter, and green vegetables are other sources of this compound.

Salts. The carbohydrates, fats, and proteins do not supply all elements necessary for a healthy continuance of life. Many elements must be supplied to the blood and to the tissues in the form of salts. Sodium chloride is a normal component of the blood. In much smaller concentrations it is found in all the fluids of the body. Sodium chloride is the only salt that is not present in sufficient quantities in the foods we commonly use. We share with the herbivorous animals the experience of salt-hunger. Carnivorous animals do not crave salt, for they obtain plenty of sodium chloride from the blood of their prey.

Sodium, calcium, magnesium, potassium, phosphorus, sulfur, chlorine, iron, and iodine are the principal inorganic constituents of the body. Calcium phosphate is the chief inorganic component of bone. Iodine is found in many tissues of the body, especially in the thyroid gland. Iodine deficiency is a common cause of goiter. Iron and sulfur are constituents of the red corpuscles of the blood. These elements are needed only in small quantities in our diet but we could not live without them.

The average elementary composition of the body is approximately as indicated in the table below.

AVERAGE ELEMENTARY COMPOSITION OF THE HUMAN BODY

Element	Per cent in body	Element	Per cent in body
Oxygen.....	65	Potassium.....	0.3
Carbon.....	18	Sulfur.....	0.3
Hydrogen.....	10	Sodium.....	0.2
Nitrogen.....	3	Chlorine.....	0.2
Calcium.....	1.5	Other elements.....	0.5
Phosphorus.....	1.0		

Questions and Exercises

1. Name the two principal functions of foods.
2. Name three classes of foods.
3. What is a carbohydrate; a fat; a protein?
4. What quantity of heat is released when 1 lb. of a carbohydrate is oxidized to carbon dioxide and water? Express the answer in kilogram-calories.
5. What is a vitamin? Why are vitamins valuable as constituents of the diet?
6. Name some foods that are rich in the following classes of compounds: (a) carbohydrates, (b) fats, (c) proteins.
7. How many calories are required to heat 650 g. of water from 20° to 85°C.?
8. What weight of sugar must be burned to melt 1 lb. of ice? (The heat of fusion of ice is 79 cal. per gram. A pound is equal to 453.59 g.)
9. Calculate the weight of water required to hydrolyze 171 g. of cane sugar.
10. Calculate the weight of calcium in your own body.

UNIT XXII

Radioactivity and the Transmutation of Elements

PART 1

Radioactive Elements

The hydrogen atom is the simplest and the uranium atom is the most complicated of all the atoms. The atomic weight of uranium is 238; its atomic number is 92; and we believe its nucleus to be composed of 92 protons and 146 neutrons. Progressing from hydrogen to uranium, the atoms of the different elements contain more and more protons and neutrons, and with increasing numbers of protons and neutrons in the nuclei of the atoms the elements become less stable. There seems to be a limit to the number of protons and neutrons that can be held together in the central part, or nucleus, of an atom, and this limit is reached in uranium. As this limit is approached, the forces holding the protons and neutrons together become weaker.

The nuclei of the heavy elements are less stable than those of the light elements, and the elements that are heavier than lead have a tendency to break up, forming lighter elements. This change, or transformation, of heavier to lighter atoms takes place slowly but at a constant rate, and the rate is the same whether the element is in the free state or in a compound. Elements having nuclei that break up or disintegrate in this way are called *radioactive elements*.

Properties of the radioactive elements. The radioactive elements give off three kinds of rays, known as alpha, beta, and gamma rays. The α -rays (*alpha particles*) are positively charged, and it has been proved that they are nuclei of helium atoms with a mass equal to that of two protons plus two neutrons and with an electrical charge twice as great as the charge on a hydrogen ion—that is, a +2 charge. Each of these particles becomes a helium atom by capturing two electrons, which it may take from almost any molecule or atom with which it comes in contact. The alpha particles are ejected from the nucleus of the radium atom, sometimes with very high velocities. The fastest of these particles move with an initial velocity of about 13,000 miles per second.

The β -rays, or *beta particles*, are electrons. These electrons, like the alpha particles, are ejected *from the nucleus* of the radioactive atom with enormous velocities. The beta particles are negatively charged. They have approximately $\frac{1}{7500}$ the weight of the positively charged alpha particles.

The γ -rays (*gamma rays*) are not charged, and it has been shown that they are light rays of very high vibration frequencies. X rays are light rays of very short wave lengths (high frequencies), but the gamma rays have much shorter wave lengths than those of the X rays. Having greater frequencies or shorter wave lengths than X rays, the gamma rays are able to penetrate solid matter to

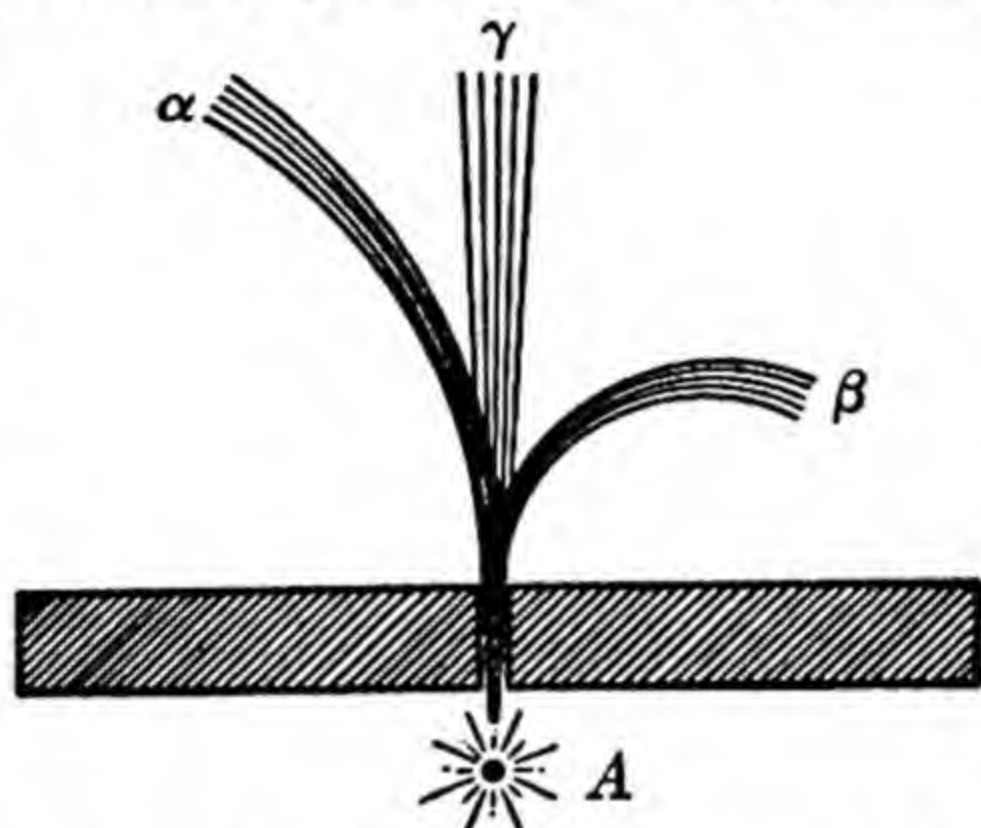


Fig. 175. Effect of a magnetic field on the rays emitted by a radioactive substance.

greater depths. Gamma rays are able to penetrate several inches of solid lead.

The different properties of the alpha, beta, and gamma rays can be demonstrated by an experiment sketched in Fig. 175. The radioactive substance is placed at A. The alpha, beta, and gamma rays are emitted in all directions, but if a heavy lead plate with a slit in it is placed over the substance, the rays will pass through the slit only. A magnet placed in the path of the rays deflects the charged particles in curved paths, as shown in the figure, while the uncharged gamma rays pass on in a straight line. The speed of a particle can be determined by the curvature of its path. The faster the particle moves, the less time it spends in the magnetic field, and the less its path is bent. The paths of alpha and beta particles are determined by electrical instruments or by the effects of the rays on photographic plates.

What happens to the radium nucleus? Radium has an atomic weight of 226 and an atomic number of 88. It has two valence electrons and belongs to the second group of the periodic system. Its chemical reactions are similar to those of calcium, strontium,

and barium. From time to time radium atoms disintegrate, and from each atom that undergoes this spontaneous change an alpha particle is released. Since an alpha particle has a mass of 4 and a charge of $+2$, the nucleus of the disintegrating radium atom loses this same mass and charge. The resulting nucleus, then, has a mass of 222 ($226 - 4$) and a plus charge of 86 ($88 - 2$). Before the nucleus of the radium atom released the alpha particle, there were 88 outside electrons about it, and a charge of $+88$ on the nucleus. After the expulsion of the alpha particle the charge on the nucleus is only $+86$, and two electrons must escape from the valence shell to preserve the neutrality of the atom as a whole. The newly formed atom, therefore, has no valence electrons. It belongs to the zero group in the periodic system. The element formed in this process is the rare gas radon.

The decomposition of radium takes place so slowly that in 1580 years only half of it is converted into radon and helium. This time, 1580 years, is called the *half-life* of radium. Half of the remaining portion is decomposed in the next 1580 years, and so on. This mode of decomposition applies to any sample of the element, whether large or small.

The gas radon is itself radioactive, and like radium it gives off alpha particles, but its half-life is only 3.85 days. As in the disintegration of radium, the nuclear charge of the radon atom and its number of outside electrons are decreased by two. (See table, page 507.) The new element formed from radon is called *radium A*, which belongs to the sixth group of the periodic system.

Radium B decomposes spontaneously, but instead of losing an alpha particle it gives off a beta particle (an electron). When the nucleus loses a beta particle or electron, its positive charge increases by one unit, and one electron must be added to the valence shell to make the atom, as a whole, neutral. It can acquire a valence electron from almost any substance with which it comes in contact. The mass of the atom (atomic weight) is not changed in this process, for the mass of the escaping electron is negligible. The electron ejected from the nucleus does not attach itself as a valence electron; it is moving with too great a velocity to be captured in this way. The new valence electron is acquired from some other atom or molecule. The electron ejected from the nucleus of a radium B atom comes from a neutron which breaks into a proton and an electron or β -particle. The proton remains in the nucleus of the atom, increasing the positive charge in the nucleus by one unit without appreciably changing the mass of the atom.

The process of spontaneous decomposition of radioactive elements continues until lead is produced. Lead is not radioactive.

Radium is produced from uranium through a long series of changes, and it is found only in uranium ores. The best radium ore is found in the Belgian Congo in Africa, and only about 3 g. of radium are contained in 10,000,000 g. of the ore.

THE CONVERSION OF RADIUM INTO RADIUM C
RADIUM → RADON → RADIUM A → RADIUM B → RADIUM C
(Valence electrons in heavy type)

Element	Nucleus			Electrons in shells outside nucleus						
	Number of protons + neutrons (atomic weight)	Number of neutrons	Net positive charge (atomic number)	1st shell	2nd shell	3rd shell	4th shell	5th shell	6th shell	7th shell
Radium	226	138	88	2	8	18	32	18	8	2
Loss of 1 Alpha Particle from Nucleus and 2 Electrons from Outside Shell Yields										
Radon	222	136	86	2	8	18	32	18	8	none
Loss of 1 Alpha Particle from Nucleus and 2 Electrons from Outside Shell Yields										
Radium A	218	134	84	2	8	18	32	18	6	
Loss of 1 Alpha Particle from Nucleus and 2 Electrons from Outside Shell Yields										
Radium B	214	132	82	2	8	18	32	18	4	
Loss of 1 Beta Particle from Nucleus and Gain of 1 Electron by Outside Shell Yields										
Radium C	214	131	83	2	8	18	32	18	5	

Lead is formed from uranium through a series of 15 or more changes. Thorium is another element that breaks up spontaneously with the ultimate formation of lead.

The age of the earth. By laboratory methods it has been shown that each gram of uranium yields 1.26 ten-billionths of a gram of lead per year. From the quantity of lead found in a

crystal of uranium mineral, it is possible to calculate how long the crystal has been in existence, or how long ago the crystal was formed from molten material. By this method it has been estimated that some of these minerals were crystallized over a billion years ago. Samples from the Black Hills of South Dakota have an age of 1700 million years, and some samples from Russia are 2000 million years old.

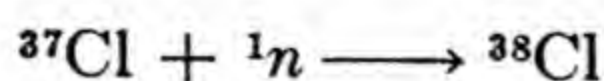
It is possible also to calculate the amount of helium gas which is formed per year from each gram of uranium. There are minute quantities of helium in the interior of crystals of uranium ores. Each alpha particle escaping from the nucleus of a uranium atom becomes, on neutralization by two electrons, a helium atom, and the helium atoms formed in this way in the interior of a rock crystal are unable to escape. By heating the mineral to its melting point the helium can be driven out and measured. Since some helium atoms may have escaped from the crystals of the mineral during the long ages of its existence, the age of the crystals as determined in this way is a minimum age. Even so, samples have been found that indicate an age of about a billion years.

Artificial transmutations. Neutrons can be driven out of beryllium by mixing powdered beryllium with a little radium or radium bromide. The radium gives off alpha particles, and some of these are absorbed by the beryllium. Each beryllium atom which catches an alpha particle is converted into carbon, and at the same time a neutron escapes:



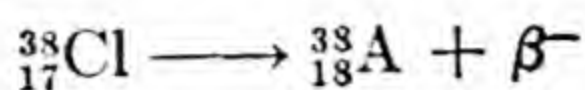
The equation states that a beryllium atom (atomic weight 9) combines with a helium atom (atomic weight 4), forming a carbon atom (atomic weight 12) and releasing a neutron (atomic weight 1).

If the mixture of beryllium and radium is surrounded by common salt, some of the sodium atoms and chlorine atoms acquire more than their usual quotas of neutrons and become unstable isotopes of sodium and chlorine. Radio-active chlorine is produced as follows:



A chlorine atom having an atomic weight of 38 is unstable. In 37 minutes half of any quantity of ${}^{38}\text{Cl}$ has disappeared, and in 37 minutes more, half of the remainder has changed. No matter how much of it is on hand at any moment, half of it is gone in 37 minutes. We say that the half-life of this isotope of chlorine is 37 minutes. The change involves the loss of an electron from the nucleus of the chlorine atom. One of the neutrons breaks into a proton and a beta particle. The proton is retained in the nucleus,

and the beta particle moves out. This escape of a beta particle from the nucleus changes the charge on the nucleus from 17 to 18, and the result is the formation of a different element, in this case argon. The newly formed atom acquires an electron from its surroundings to complete its outer shell.



Graphically, the change from chlorine to argon may be represented as follows:

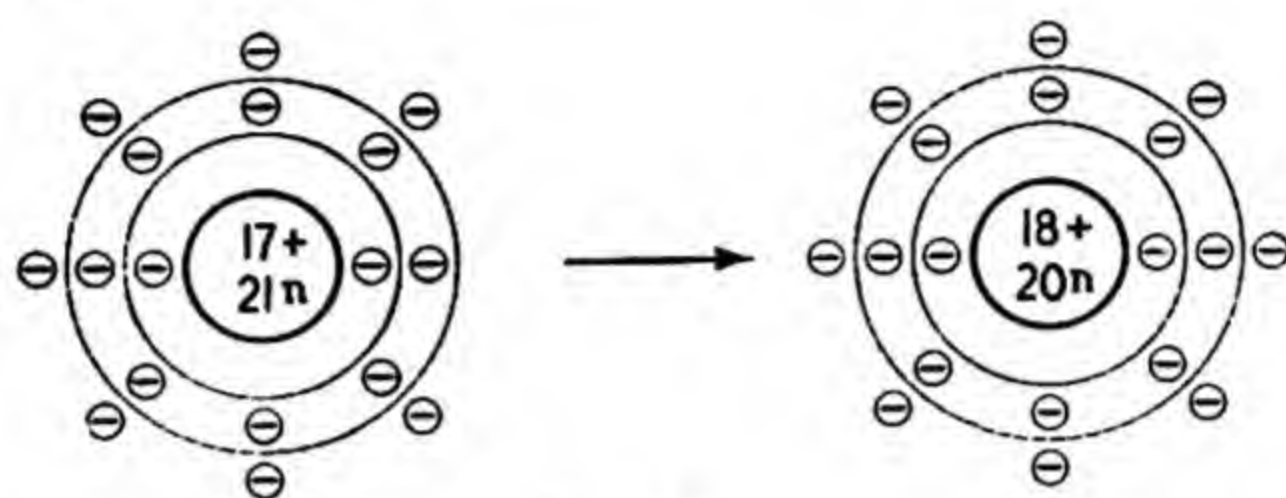


Fig. 176.

Chlorine atom ${}_{17}^{38}\text{Cl}$
Atomic number 17
Atomic weight 38

Argon atom ${}_{18}^{38}\text{A}$
Atomic number 18
Atomic weight 38

We are now independent of the *natural* sources of alpha particles, deuterons, and other high-speed bullets which can be used successfully in the bombardment of stable atoms. With the aid of the cyclotron, invented by Lawrence at the University of California, we can impart high velocities to protons, deuterons, or alpha particles; and indirectly, through the use of these projectiles, we can obtain neutrons at high or low speeds. When these particles strike the nuclei of ordinary atoms, artificial radioactivity is induced and atoms of entirely different elements are the ultimate products. In this way many transmutations have been accomplished.

Deuterons are deuterium ions, also called heavy hydrogen ions. They are represented by the symbol D^+ or ${}^2\text{H}^+$. They are obtained from heavy water (deuterium oxide) which was described on page 73.

In the type of change illustrated by the examples given above, the transmutations are accomplished by small changes. The mass of an atom is changed by 0, 1, 2, 3, or 4. A surprising result was observed in 1939 when uranium was subjected to bombardment with neutrons. A uranium atom of atomic weight 235 takes up a neutron and forms a very unstable atom which explodes, yielding fragments of approximately equal masses, and the energy released in this process is enormous. Iodine, bromine, antimony, tellurium, and barium are found among the explosion

products. The uranium atoms do not all break up in the same way, and therefore many atoms can be detected among the decomposition products. A new element, plutonium (atomic number 94), has been made from uranium 238 by bombardment with neutrons. Plutonium, like uranium 235, is subject to fission or disintegration. It is estimated that the energy released in the fission of uranium or plutonium is approximately 20,000,000 times as great as the energy released in the explosion of an equal weight of TNT. The first controlled use of atomic energy was demonstrated at Hiroshima, Japan, on August 5, 1945. A single "atomic energy" bomb destroyed more than half a great city. We may soon see the development of many peacetime uses of this new source of energy.

Questions and Exercises

1. What are (a) alpha rays, (b) beta rays, (c) gamma rays?
2. Which elements resemble radium in chemical properties?
3. What is meant by the term "radioactive"?
4. Why are radium salts expensive?
5. Do radium salts yield alpha, beta, and gamma rays, or is this a property of the free metal only?
6. Name two elements that are formed in the spontaneous decomposition of radium.
7. Have chemists been able to stop the decomposition of elements heavier than lead or to start a similar process of disintegration in elements lighter than lead?
8. The half-life of radium is 1580 years. If a sample of radium weighs 1 mg. at the present time, what will it weigh 1580 years from now? What will it weigh 3160 years from now?
9. Do isotopes differ in chemical properties? Do they differ in atomic weights? Do they differ in atomic numbers? Do isotopes have the same number of valence electrons? Do they have the same number of protons in the nucleus? Do they have the same number of neutrons in the nucleus?
10. If a proton were knocked out of the nucleus of an aluminum atom by bombardment with an alpha particle and if the alpha particle did not attach itself to the aluminum atom, what would be formed?
11. Outline two methods by which the time that has lapsed since the solidification of the earth can be determined.
12. If an atom of an element in the fourth group of the periodic system loses a beta particle from the nucleus, it forms an atom of some element of the fifth group. Explain.

APPENDIX

The Metric System

The metric system is used in all scientific laboratories for measuring volumes, lengths, and weights. In this system each unit is equal to one-tenth of the next larger one. Such a system is called a "decimal system." Our currency is based upon this system, but we have not adopted, for commercial use, a decimal system for the measurement of weight, volume, or length. The United States and Great Britain are practically the only civilized countries which do not use the metric system for all kinds of measurement. Anyone who uses a radio is familiar with some of the units in this system, for the wave lengths are given in meters or kilometers, and the frequencies are given in kilocycles.

Linear measurements. The meter is taken as the unit of length. It is equal to 39.37 inches. *The International Standard Meter* is the distance between two lines, at 0°C., on a platinum-iridium bar deposited at the International Bureau of Weights and Measures near Paris, France. A similar bar is kept by the Bureau of Standards at Washington, D.C. Inexpensive replicas of the standard bar are available in many laboratories. The meter is divided into tenths, these tenths into tenths, and so on. The following list shows the decimals and multiples of the meter and their names:

10 millimeters (mm.)	= 1 centimeter (cm.)
10 centimeters	= 1 decimeter (dm.)
10 decimeters	= 1 meter (m.)
10 meters	= 1 dekameter (Dm.)
10 dekameters	= 1 hektometer (Hm.)
10 hektometers	= 1 kilometer (Km.)

A millimeter is $\frac{1}{1000}$ of a meter; a centimeter is $\frac{1}{100}$ of a meter; a decimeter is $\frac{1}{10}$ of a meter. A dekameter is 10 meters; a hektometer is 100 meters; a kilometer is 1000 meters.

The relationships between the metric system and our ordinary system are as follows:

1 meter	= 39.37 inches
1 decimeter	= 3.937 inches
1 centimeter	= 0.3937 inch
1 millimeter	= 0.03937 inch
1 inch	= 2.54 centimeters

Measurement of mass. The *kilogram* is the standard unit of weight. The *International Standard kilogram* is the weight of a mass of platinum-iridium alloy deposited at the International Bureau of Weights and Measures.

Weights of small quantities are expressed in grams. A *gram* is equal to the weight of 1 cubic centimeter of water at 4°C. A kilogram is 2.2 pounds, and 1 pound is equal to 0.454 kilograms.

10 milligrams (mg.)	= 1 centigram (cg.)
10 centigrams	= 1 decigram (dg.)
10 decigrams	= 1 gram (g.)
10 grams	= 1 dekagram (dkg.)
10 dekagrams	= 1 hektogram (hg.)
10 hektograms	= 1 kilogram (kg.)

Measurement of volume. The liter is the unit of volume. The *liter* is equal to a cubic decimeter. It is equal also to the quantity of distilled water which, at its maximum density (4°C.) weighs 1 kilogram.

Since a liter contains 1000 cubic centimeters, 1 cubic centimeter of water at 4°C. weighs 1 gram. A liter is approximately equal to 1.06 quarts. One quart is equal to 0.95 liter.

10 milliliters (ml.)	= 1 centiliter (cl.)
10 centiliters	= 1 deciliter (dl.)
10 deciliters	= 1 liter (l.)
10 liters	= 1 dekaliter (Dl.)
10 dekaliters	= 1 hektoliter (Hl.)
10 hektoliters	= 1 kiloliter (Kl.)

A cubic centimeter is the volume of a cube 1 centimeter in each dimension. A thousand cubic centimeters make 1 liter.

Measurement of temperature. Scientists use the Centigrade thermometer for measuring temperature. The fixed points on this scale are:

0°C.	= freezing point of water
100°C.	= boiling point of water.

The space between the two fixed points is divided into 100 degrees, and, in the more accurate thermometers, each of these is divided into tenths and hundredths of a degree.

The only scientific laboratory that still uses the Fahrenheit thermometer is the United States Weather Bureau. The zero point on a Fahrenheit thermometer is 32° below the freezing point of water. The boiling point of water is at 212°F. The space between these two fixed points is divided into 180 equal parts representing degrees.

Since the interval between the freezing point and the boiling point of water is divided into 100 degrees on the Centigrade thermometer and 180 degrees on the Fahrenheit thermometer, the degrees on the two instruments are different. One Centigrade degree is equal to $\frac{180}{100}$ or $\frac{9}{5}$ Fahrenheit degrees. A Fahrenheit degree is equal to $\frac{5}{9}$ of a Centigrade degree.

Suppose the temperature as read on a Fahrenheit thermometer is 72° . What is the corresponding Centigrade temperature? The reading shows 72° above zero, but it is only 40° ($72 - 32$) above the freezing point of water. Now 40 Fahrenheit degrees are equal to $40 \times \frac{5}{9}$ or 22.2 Centigrade degrees. The corresponding Centigrade temperature is, therefore, 22.2° .

Let us make a conversion the other way. Find the Fahrenheit temperature corresponding to 50°C . This given temperature is 50 Centigrade degrees above the freezing point of water. It would be $\frac{9}{5} \times 50$ or 90 Fahrenheit degrees above the freezing point of water. But the freezing point of water is 32° above zero on the Fahrenheit scale. We must, therefore, add 32 to the 90, and our corresponding temperature is 122°F .

The following formulas may be used in making such conversions:

$$C = \frac{5}{9}(F - 32) \quad \text{and} \quad F = \frac{9}{5}C + 32$$

VAPOR PRESSURES OF WATER

Temperature		Pressure (mm. of mercury)	Temperature		Pressure (mm. of mercury)
Fahrenheit	Centigrade		Fahrenheit	Centigrade	
32°	0°	4.6	71.6°	22°	19.7
41	5	6.5	73.4	23	20.9
46.4	8	8.0	75.2	24	22.2
48.2	9	8.6	77.0	25	23.6
50.0	10	9.2	78.8	26	25.1
51.8	11	9.8	80.6	27	26.5
53.6	12	10.5	82.4	28	28.1
55.4	13	11.2	84.2	29	29.8
57.2	14	11.9	86.0	30	31.5
59.0	15	12.7	87.8	31	33.4
60.8	16	13.5	89.6	32	35.4
62.6	17	14.4	91.4	33	37.4
64.4	18	15.4	93.2	34	39.6
66.2	19	16.3	95.0	35	41.8
68.0	20	17.4			
69.8	21	18.5	212.0	100	760.0

WEIGHT OF ONE LITER OF VARIOUS GASES IN GRAMS
UNDER STANDARD CONDITIONS

Acetylene.....	1.1730	Chlorine.....	3.2140	Nitric oxide.....	1.3402
Air.....	1.2929	Helium.....	0.1785	Nitrous oxide...	1.9778
Ammonia.....	0.7710	Hydrogen.....	0.0898	Oxygen.....	1.4290
Argon.....	1.7832	Hydrogen chloride.	1.6392	Phosgene.....	4.4172
Carbon dioxide...	1.9769	Hydrogen sulfide..	1.5390	Sulfur dioxide...	2.9269
Carbon monoxide..	1.2504	Methane.....	0.7168		

APPROXIMATE MELTING POINTS OF METALS AND A FEW NONMETALS
(DEGREES CENTIGRADE)

Aluminum.....	658	Cobalt.....	1490	Molybdenum.....	2620
Antimony.....	630	Copper.....	1083	Nickel.....	1452
Barium.....	850	Gold.....	1063	Phosphorus (white)..	44
Beryllium.....	1350	Iodine.....	113	Platinum.....	1770
Bismuth.....	271	Iridium.....	2350	Potassium.....	63
Boron.....	2300	Iron.....	1530	Silicon.....	1427
Cadmium.....	321	Lead.....	327	Silver.....	961
Calcium.....	851	Lithium.....	179	Sodium.....	97
Carbon.....	3500	Magnesium.....	650	Sulfur (rhombic)....	113
Cesium.....	28	Manganese.....	1220	Tin.....	232
Chromium.....	1545	Mercury.....	-39	Tungsten.....	3387

OXIDATION-REDUCTION POTENTIALS
(At molar concentration and 25°C.)

	<i>Reaction</i>	<i>E°</i>
K	$\rightarrow \text{K}^+ + e^-$	+2.92
Ca	$\rightarrow \text{Ca}^{++} + 2e^-$	+2.87
Na	$\rightarrow \text{Na}^+ + e^-$	+2.71
Mg	$\rightarrow \text{Mg}^{++} + 2e^-$	+2.34
Al	$\rightarrow \text{Al}^{+++} + 3e^-$	+1.67
Zn	$\rightarrow \text{Zn}^{++} + 2e^-$	+0.76
Fe	$\rightarrow \text{Fe}^{++} + 2e^-$	+0.44
Pb	$\rightarrow \text{Pb}^{++} + 2e^-$	+0.13
H ₂	$\rightarrow 2\text{H}^+ + 2e^-$	0.00
Cu	$\rightarrow \text{Cu}^{++} + 2e^-$	-0.34
Cu	$\rightarrow \text{Cu}^+ + e^-$	-0.52
2I ⁻	$\rightarrow \text{I}_2 + 2e^-$	-0.53
Ag	$\rightarrow \text{Ag}^+ + e^-$	-0.80
Hg	$\rightarrow \text{Hg}^{++} + 2e^-$	-0.85
ClO ₃ ⁻ + H ₂ O	$\rightarrow 2\text{H}^+ + \text{ClO}_4^- + 2e^-$	-1.00
2Br ⁻	$\rightarrow \text{Br}_2 + 2e^-$	-1.06
2H ₂ O	$\rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$	-1.23
2Cl ⁻	$\rightarrow \text{Cl}_2 + 2e^-$	-1.36
Au	$\rightarrow \text{Au}^{+++} + 3e^-$	-1.42
2F ⁻	$\rightarrow \text{F}_2 + 2e^-$	-2.85

PROPERTIES OF SULFIDES

Sulfides	Formula	Color	Conditions for precipitation with H_2S	Dissolves in
Calcium sulfide	CaS	Gray	—	Decomposed by water to give $Ca(OH)_2$ and H_2S
Ferrous sulfide	FeS	Black	Alkaline solution	Dilute acids
Zinc sulfide	ZnS	White	Alkaline solution	Dilute acids
Cadmium sulfide	CdS	Yellow	Acid or alkaline solution	Concentrated nitric acid
Copper sulfide	CuS	Black	Acid or alkaline solution	Concentrated nitric acid
Silver sulfide	Ag_2S	Black	Acid or alkaline solution	Concentrated nitric acid
Mercuric sulfide	HgS	Black	Acid or alkaline solution	Aqua regia
Arsenic trisulfide	As_2S_3	Yellow	Acid or alkaline solution	Concentrated nitric acid or sodium sulfide or ammonium sulfide solution
Antimony trisulfide	Sb_2S_3	Orange-red	Dilute acid or alkaline solution	Concentrated acids, sodium sulfide, or ammonium sulfide solution
Stannous sulfide	SnS	Brown	Dilute acid or alkaline solution	Concentrated acids or sodium or ammonium polysulfide (sulfide plus dissolved sulfur)
Stannic sulfide	SnS_2	Yellow	Dilute acid or alkaline solution	Concentrated acids or sodium sulfide or ammonium sulfide solution

Index

A

Absolute temperatures, 92
 Absolute zero, 91, 92
 Acetaldehyde, 480
 Acetic acid, 215, 219, 480
 Acetone, 474, 480
 Acetylene, 471
 Acid anhydride, 208
 Acids, 207, 221
 as source of hydrogen, 56, 208
 composition, 207
 occurrence, 207
 preparation, 196, 208
 properties, 195
 reactions, 195, 208
 Acid salts, 211
 Acid sodium sulfate, 212
 Adsorption, 243
 Age of the earth, 507
 Air, 32, 42
 composition, 35
 liquid, 37, 42
 pressure, 33
 weight, 32
 Alcohols, 475
 Aldehydes, 479
 Alkali metals, 164, 175
 Alkaline earth metals, 344, 362
 Alkane series, 460
 Alkene series, 466
 Alkyl radicals, 462
 Alkyne series, 471
 Allegheny metal, 446
 Allotropic forms:
 carbon, 288
 oxygen, 50
 phosphorus, 276, 277
 sulfur, 325
 tin, 422
 Alloys:
 aluminum, 369
 antimony, 286
 arsenic, 284
 beryllium, 345
 cadmium, 400
 chromium, 432, 446
 cobalt, 446, 452
 copper, 379
 gold, 391
 iridium, 457
 iron, 446, 447
 lead, 427
 magnesium, 347
 manganese, 438, 446
 molybdenum, 434
 nickel, 446, 453
 palladium, 457
 platinum, 457
 tin, 423
 tungsten, 435, 446
 Alpha particles, 504
 Aluminum, 364, 367
 alloys, 369

Aluminum (*Cont.*):
 alums, 371
 atom, 112
 hydroxide, 369
 occurrence, 367
 oxide, 370
 preparation, 367
 properties, 364, 368
 salts, 371
 Alums, 371
 Alundum, 367
 Amalgamation process, 390
 Amalgams, 401
 Ammonia, 252
 commercial preparation, 254
 compounds, 257
 occurrence, 252
 oxidation, 262
 preparation, 252, 254
 properties, 252
 uses, 256
 Ammonium:
 hydroxide, 209, 215, 220, 253
 salts, 257
 Amorphous solids, 24, 288
 Amphoteric substances, 373
 aluminum, 373
 boron, 373
 chromium, 433
 manganese, 438
 tin, 424
 zinc, 397
 Analysis, 64
 Anode, 217
 Anthracite coal, 291
 Antimony, 246, 275, 285
 occurrence, 285
 oxide, 286
 preparation, 286
 properties, 275, 286
 sulfide, 285, 286, 515
 uses, 286
 Apatite, 349
 Aqua regia, 264, 331, 456
 Aragonite, 350
 Arc process, 263
 Argon, 36, 126, 132
 atomic structure, 113, 132
 occurrence, 36
 Arizonite, 321
 Aromatic compounds, 472
 Arrhenius, Savante August, 218
 Arsenic, 246, 275, 284
 compounds, 285
 Marsh test for, 285
 occurrence, 284
 properties, 275, 284
 sulfide, 435, 515
 uses, 284
 Arsine, 285
 Artificial ice, 257, 335
 Asbestos, 346
 Ascorbic acid, 502
 Atmosphere, 32

Atmospheric pressure, 33, 90
 Atomic hydrogen torch, 59
 Atomic nucleus, 108, 110
 Atomic number, 110
 Atomic structure, 108, 132
 and chemical reactions, 121
 Atomic weights, 103, 104, 105, 110
 table, approximate, front cover
 table, exact, back cover
 Atoms, 103, 104
 nature, 5
 structures, 107, 132
 Autoclave, 71
 Avogadro's law, 99
 Avogadro's number, 152

B

Bakelite, 479
 Baking powders, 305
 Baking soda, 302, 305
 Balancing equations, 136
 Barite, 324, 359
 Barium, 344, 359
 compounds, 359
 occurrence, 359
 preparation and properties, 359
 Barometer, 33
 Bases, 169, 207, 209, 221
 preparation, 209
 Basic anhydrides, 209
 Basic salts, 376
 Bauxite, 367
 Becquerel, Henri, 107, 361
 Benzene, 472
 Benzine, 472
 Beriberi, 500
 Beryl, 344
 Beryllium, 344
 Beryllium atom, 111
 Berzelius, J. J., 342
 Bessemer converter, 377, 443
 Bessemer process, 443
 Beta particles, 505
 Betts process, 426
 Bicarbonates, 302, 308, 309
 Bismuth, 246, 275
 occurrence, 286
 properties, 275, 286
 uses, 286
 Bituminous coal, 291
 Blast furnace, 441, 442
 Bleaching powder, 185, 351
 Blister copper, 378
 Bluestone, 380
 Blue vitriol, 380
 Bohr, Niels, 109
 Boiler scale, 355
 Boiling point, 69
 elevation, 86
 of solutions, 86, 87, 216
 of water, 25
 Bone black, 293
 Borax, 364, 365
 Borax beads, 366
 Bordeaux mixture, 380
 Boric acid, 364, 365
 Boron, 364, 373
 atom, 112, 115
 Boyle's law, 89
 Brand, Hennig, 276
 Brass, 379, 396
 Bromic acid, 204
 Bromine, 180, 187
 occurrence, 188

Bromine (*Cont.*):
 preparation, 188
 properties, 189
 test for, 191, 201
 Brownian movement, 237
 Bunsen, Robert, 178
 Bunsen burner, 46
 Burettes, 233
 Burning, nature of, 44, 45
 Butadiene, 469
 Butane, 461, 462
 Butylene, 468

C

Cadmium, 394, 400
 compounds, 400
 extraction from ores, 400
 properties and uses, 394, 400
 sulfide, 400
 yellow, 400
 Calcite, 349
 Calcium, 344
 action of, on water, 55
 atom, 112, 113
 bicarbonate, 354
 carbide, 471
 carbonate, 349, 354
 chloride, 352
 compounds, 349
 hydroxide, 55, 351
 occurrence, 349
 oxide, 350
 phosphate, 279, 491
 preparation, 349
 properties, 349
 sulfate, 352, 355
 sulfide, 515
 Calculations, 146, 156, 160
 Calomel, 402
 Calorie, 69, 495
 Cane sugar, 484, 496
 Carat, 289, 390
 Carbohydrates, 484, 495
 Carboloy, 435, 452
 Carbon, 288
 acids, 296, 302
 amorphous forms, 291
 atom, 112
 compounds, 459
 crystalline forms, 289
 occurrence, 288
 properties, 289
 tetrachloride, 474
 Carbonates, 302, 308
 Carbon dioxide, 36, 295, 297
 liquid, 304
 molecule, 297
 occurrence, 36, 298
 preparation, 298
 properties, 299, 301
 solid, 301
 test for, 301
 uses, 300
 Carbonic acid, 207, 302
 salts of, 308
 Carbon monoxide, 295
 detector, 296
 molecule, 295
 occurrence and properties, 295
 preparation, 296
 reducing action, 297
 Carbon tetrachloride, 474
 molecule, 127
 Carborundum, 312

- Carlsbad Caverns, 358
 Carnallite, 172, 346
 Carter process, 428
 Cassiterite, 422
 Cast iron, 442
 Castner process, 165
 Catalyst, 41, 272, 336
 Cathode, 217
 Caustic soda, 169
 Cavendish, Henry, 52, 53
 Celestite, 359
 Cellophane, 485
 Cells, electric, 408
 Daniell, 409
 dry, 410
 voltaic, 409
 wet, 408
 Cellulose, 485
 nitrate, 485
 Cement, 316
 Centigrade thermometer, 92, 512, 513
 Cerium, 135, 322
 Cesium, 134, 164, 172, 173, 175
 Chamber process, 336
 Change:
 chemical, 26
 physical, 27
 Charcoal, 292
 Charles's law, 91
 Chemical calculations, 146
 Chemical change, 26
 Chemical equations, 40, 136
 Chemical properties, 26
 Chemical reactions:
 and atomic structure, 121
 speeds of, 272
 Chile saltpeter, 169, 265
 Chlorate, 203
 Chloric acid, 203
 Chloride of lime, 185, 351
 Chlorination process for gold, 389
 Chlorine, 180
 atom, 113, 114, 122
 molecule, 101, 126
 preparation, 181
 properties, 183
 transportation, 183
 uses, 184
 Chloroform, 474
 Chloroplatinic acid, 456
 Chlorous acid, 203
 Chromates, 433
 Chrome alum, 371
 Chrome yellow, 428
 Chromite, 431
 Chromium, 431
 alloys, 432
 compounds, 432
 extraction, 431
 occurrence, 431
 preparation, 431
 properties, 432
 uses, 432
 Chromol, 432
 Cinnabar, 401
 Citric acid, 207
 Clay, 371
 Clinker, 318
 Coagulation of colloids, 242
 Coal, 291
 gas, 487
 Cobalt, 439, 452
 alloys, 446, 452
 compounds, 452
 extraction, 452
 Cobalt (*Cont.*):
 occurrence, 452
 properties and uses, 439, 452
 steel, 446
 Cobaltite, 452
 Cohesion, 17
 Coin silver, 383
 Coke, 292
 Colemanite, 364
 Collodion, 485
 Colloidal palladium, 457
 Colloidal sulfur, 326
 Colloid mill, 240
 Colloids, 237
 adsorption by, 243
 coagulation, 242
 hydrophobic, 241
 hydrophylic, 241
 lyophobic, 241
 lyophylic, 241
 preparation, 240
 properties, 237
 uses, 243, 244
 Combination, 138
 Combining capacity, 267
 Combining volumes, 99
 Combustion, 45
 spontaneous, 45
 Complex ions:
 chromium, 433
 copper, 381, 392
 iron, 450
 silver, 382, 383, 392
 Composition, percentage, 146
 Compounds, 8, 15
 essential to animal life, 494
 Concrete, 318
 Condensation processes, 466
 Conductors, 214
 Conservation of energy, 29
 Conservation of mass, 28
 Contact process, 335
 Copper, 375
 complex ions, 392
 compounds, 380
 extraction, 376
 occurrence, 376
 properties, 375, 378, 379
 reduction of oxide, 59
 refining, 378
 sulfide, 377, 515
 tests for, 381
 uses, 379
 Copperas, 450
 Corrosive sublimate, 402
 Covalence, 125
 Cracking process, 465
 Crucible steel, 446
 Cryolite, 187, 367
 Crystal lattice, 23
 Crystals, 20
 snow, 19
 systems of, 20
 Curie, Marie, 108, 361, 435
 Curie, Pierre, 108, 361
 Cyanamide process, 256
 Cyanide process:
 for gold, 390
 for silver, 382
 Cyclotron, 115, 509

D

Dalton, John, 7
 Daniell cell, 409

Davy, Sir Humphry, 46, 165
 Debye, Peter, 218
 Decane, 462
 Decomposition, 144
 Decylene, 468
 Definite proportion, law of, 64
 Deliquescence, 84
 Density, gas, 158
 Deoxidation, 59
 Depression of freezing point, 86, 216
 Destructive distillation, 292
 Deuterium, 61, 73
 atom, 114
 Deuterons, 509
 Dewar flasks, 38
 Diamond, 288
 Dichloromethane, 474
 Dichromates, 433
 Dienes, 469
 Diffusion of gases, 57, 97
 Dispersed systems, 239
 Dissociation of strong electrolytes, 219
 Distillation:
 destructive, 292
 fractional, 464
 of water, 75
 Dithionic acid, 339
 Dodecane, 462
 Dolomite, 346
 Double decomposition, 144
 Drake, Edwin, 464
 Dry cells, 409
 Dry ice, 301
 Duralumin, 369
 Duriron, 312
 Dust, 36
 Dutch process, 429
 Dynamite, 478

E

Edison cell, 414
 Efflorescence, 83
 Electric cells, 404, 408
 Electrode potentials, 404, 419, 514
 Electrolysis, 217, 404, 415
 calcium chloride, 349
 copper sulfate, 376, 417
 cryolite, 187
 hydrochloric acid, 217, 415
 hydrofluoric acid, 187
 potassium hydroxide, 172
 silver salts, 383
 sodium chloride, 166, 181, 416
 sodium hydroxide, 165
 water, 42, 53
 Electrolytes, 215, 218
 Electromagnet, 27
 Electromotive series, 404, 514
 Electron, 7, 108
 orbits or shells, 108, 132
 theory, 103, 107
 Electrotyping, 379
 Elements, 8, 115
 abundance, 10
 allotropic forms, 50, 277, 288, 325, 422
 amphoteric, 373, 397, 424, 433, 438
 atomic numbers, 110
 atomic structure, 108, 132
 equivalent weight, 234
 essential to plant life, 490
 isotopes, 61, 113, 115
 nomenclature, 11
 number, 10
 periodic classification, 117, 119, 120

Elements (*Cont.*):
 radioactive, 504
 rare earths, 133
 symbols, 12
 table, 119, 120
 Elevation of boiling point, 86, 216
 Emery, 367
 Empirical formulas, 148
 Emulsions, 240
 Endothermic reactions, 29
 Energy:
 conservation of, 29
 in food, 497, 498
 properties, 25
 Enzymes, 274, 496
 Epsom salts, 324, 346
 Equations:
 balancing, 136
 calculations from, 149, 160
 ionic, 219, 226
 Equilibrium, 60, 253, 302
 Equivalents, 152, 234
 Equivalent weight, 152, 234
 Ergosterol, 502
 Esters, 482
 Etching glass, 198
 Ethane, 462, 467
 Ethers, 483
 Ethyl acetate, 482
 Ethyl alcohol, 476
 absolute, 477
 Ethylene, 467, 468
 Ethylene dichloride, 467
 Ethyl gasoline, 429, 466
 Exothermic reactions, 29

F

Fahrenheit thermometer, 512, 513
 Faraday, Michael, 415
 Fats, 496
 Feldspar, 13, 312
 Ferberite, 434
 Fermentation, 476
 Ferric compounds:
 chloride, 450
 ferrocyanide, 450
 hydroxide, 449
 oxide, 440
 Ferrous compounds:
 chloride, 450
 ferricyanide, 450
 hydroxide, 449
 sulfate, 450
 sulfide, 364, 515
 Fertilizers, 279, 491
 Fire extinguishers, 303, 304
 Firefoam, 303
 Fixed nitrogen, 247, 491
 Flotation process, 376, 426
 Flowers of sulfur, 326
 Fluorine, 180, 187
 atom, 112
 compounds, 188
 molecule, 126
 occurrence, 187
 preparation, 187
 properties, 188
 Fluorite, 187
 Fluorspar, 349
 Foamite, 303
 Foods, fuel value of, 498
 Fool's gold, 440
 Formaldehyde, 479
 Formalin, 479

Formation of compounds, 122
 Formica, 479
 Formic acid, 296, 480
 Formulas, 123, 129
 determination of, 147, 161
 empirical, 148
 structural, 461
 uses, 146
 Fractional distillation, 464
 Frasch process, 324
 Freezing point:
 lowering, 86
 of solutions, 86, 216
 of water, 25
 Freon, 256
 Fructose, 484, 496
 Fuels, 487
 gaseous, 487
 liquid, 489
 Fusel oil, 476
 Fusion, heat of, 72

G

Galena, 426
 Galvanized iron, 396
 Gamma rays, 505
 Gaseous fuels, 487
 Gases:
 as fuels, 487
 gram-molecular volume, 157
 kinetic theory of, 89
 laws relating to, 89, 91
 liquefaction, 37
 molecular weights, 156
 properties, 17
 relative weights, 156
 solubility in liquids, 79, 80, 82
 volume relations in reactions, 156
 weight of, liter, 158, 514
 Gasoline, 464
 Gay-Lussac's law, 99
 Gels, 243
 Germanium, 421
 German silver, 453
 Glass, 314
 Glauber's salt, 169
 Glucose, 484, 496
 Glycerine, 478
 Glycol, 477
 Gold, 375, 389
 alloys, 391
 compounds, 391
 metallurgy, 389
 occurrence, 389
 properties, 375, 390, 391
 recovery, 389
 uses, 391
 Goldschmidt process, 431
 Graham's law, 97
 Gram-atomic weight, 152
 Gram-molecular volume, 157, 160
 Gram-molecular weight, 152, 233
 Granite, 13, 313
 Graphite, 288, 290
 Green vitriol, 450
 Gun cotton, 485
 Gypsum, 349, 352

H

Haber process, 254
 Hafnium, 288, 321, 322
 Half-life, 506
 of chlorine, 508

Half-life (*Cont.*):
 of radium, 506
 of radon, 506
 Hall, Charles Martin, 367
 Halogen acids, 180, 199
 Halogens:
 bromine, 188
 chlorine, 180
 fluorine, 187
 iodine, 190
 oxygen compounds, 203
 properties, 180
 replacement series, 191
 Hard waters, 354
 Heat of fusion, 71
 Heat of neutralization, 227
 Heat of vaporization, 69
 Heavy hydrogen, 114
 Heavy water, 73
 Helium, 9, 37
 atom, 110, 111, 126, 132
 ions, 108
 Hematite, 440
 Henry's law, 82
 Heptane, 462, 463
 Héroult, 368
 Hexadecane, 462
 Hexane, 462
 Hückel, E., 218
 Humidity, 35
 relative, 36
 Hydrates, 83
 Hydration:
 of ions, 222
 water of, 83
 Hydriodic acid, 200
 Hydrobromic acid, 199
 Hydrocarbons, 459
 alkane series, 460
 alkene series, 466
 alkyne series, 471
 aromatic series, 472
 derivatives, 474, 479, 482
 dienes, 469
 nomenclature, 463
 Hydrochloric acid, 193
 preparation, 193
 properties, 194
 uses, 196
 Hydrofluoric acid, 198
 Hydrogen, 52
 atom, 104, 110
 atomic, 59
 atomic torch, 59
 detector, 413
 discovery, 52
 heavy, 61, 114
 molecule, 100, 126
 occurrence, 52
 preparation, 53
 properties, 57
 reducing action, 58
 uses, 60
 Hydrogenation, 60, 242
 Hydrogen bromide, 199
 Hydrogen chloride, 193
 Hydrogen peroxide, 63, 75
 preparation, 76
 properties, 75
 uses, 76
 Hydrogen polysulfide, 339
 Hydrogen sulfide, 329
 compounds, 330
 molecule, 330

Hydrogen sulfide (*Cont.*):

- occurrence, 329
- preparation, 329
- properties, 330
- uses, 331
- Hydrolysis, 222, 496
- Hydrophobic colloids, 241
- Hydrophylic colloids, 241
- Hydrosulfuric acid, 330
- Hydroxides, 169
- Hygroscopic substances, 84
- Hypo, 339, 387
- Hypobromous acid, 204
- Hypochlorites, 203
- Hypochlorous acid, 184, 203
- Hypoiodous acid, 204
- Hypophosphorous acid, 282
- Hyposulfurous acid, 339

I

- Inert gases, 36, 126
 - atomic structures, 111, 112, 118, 132
 - molecular structures, 37, 126
- Ink:
 - black, 450
 - sympathetic, 453
- Insulators, 214
- Invar, 446
- Iodic acid, 204
- Iodine, 180, 187
 - occurrence, 190
 - preparation, 190
 - properties, 190
 - test for, 191, 201
- Iodoform, 475
- Ionization, 214, 216, 219, 226
 - of water, 221
- Ions, 123, 216, 226
- Iridium, 455, 457
- Iron, 439
 - cast, 442
 - compounds, 449
 - galvanized, 396
 - hydroxides, 449
 - manufacture, 440
 - occurrence, 439
 - oxides, 440, 449
 - pig, 440
 - properties, 439
 - pyrite, 440
 - rusting of, 448
 - salts, 450
 - tests for, 450
 - uses, 439
 - wrought, 445
- Isobutane, 461
- Isomerism, 461
- Isooctane, 466
- Isoprene, 469
- Isotopes, 61, 113, 115

K

- Kaolin, 316, 371
- Kernel, atomic, 126
- Kerosene, 464
- Ketones, 479
- Kindling temperature, 45
- Kinetic theory, 89
- Kipp's generator, 329
- Kirchhoff, G. R., 178
- Krypton, 37, 126, 132

L

- Lampblack, 293
- Lattice, crystal, 23
- Laughing gas, 259
- Lavoisier, Antoine L., 33, 34, 39, 52
- Lawrence, E. O., 509
- Laws:
 - Avogadro's, 99
 - Boyle's, 89
 - Charles's, 91
 - definite proportions, 64
 - Gay-Lussac's, 99
 - Graham's, 97
 - Henry's, 82
 - multiple proportions, 76
 - Raoult's, 85
- Lead, 421, 426
 - acetate, 429
 - alloys, 427
 - basic carbonate, 428
 - carbonate, 428
 - Carter process, 428
 - chromate, 428, 433
 - dioxide, 427
 - Dutch process, 429
 - extraction, 426
 - occurrence, 426
 - oxides, 427
 - properties and uses, 421, 427
 - red, 428
 - sulfate, 429
 - sulfide, 426, 429
 - tetraethyl, 429, 466
 - white, 428
- Lead glass, 315
- Lead storage battery, 412
- Leavening, 305
- Lignite, 291
- Lime, 351
 - airslaked, 351
- Lime glass, 315
- Limestone, 311
 - caves, 358
- Limewater, 351
- Limonite, 440
- Linear measurements, 511
- Liquid air, 37, 42
- Liquid fuels, 489
- Liquid state, 18
- Litharge, 427
- Lithium, 164, 172, 173
 - atom, 111, 115
- Lithopone, 359, 398
- Lodestone, 440
- Lowering of freezing point, 86
- Lubricating oils, 465
- Lye, 54, 170
- Lyophobic colloids, 241
- Lyophylic colloids, 241

M

- Magnalium, 369
- Magnesite, 346
- Magnesium, 344, 345
 - atom, 112
 - fluoride, 123, 124
 - nitride, 347
 - occurrence, 345
 - oxide, 123
 - preparation, 346
 - properties, 347
 - sulfate, 346, 355
 - uses, 347

Magnetic iron oxide, 55
 Magnetite, 440
 Malachite, 376
 Maltose, 476
 Manganese, 437
 alloys, 438, 446
 compounds, 438
 dioxide, 41, 182, 437, 438
 extraction, 437
 occurrence, 437
 properties, 437
 uses, 438
 Manganese steel, 446
 Marsh gas, 461
 Marsh test for arsenic, 285
 Matches, 1, 277
 Matte, 377
 Matter, 4
 conservation, 28
 physical states, 17
 properties, 25
 Measurement:
 of length, 511
 of mass, 512
 of temperature, 512
 of volume, 512
 Melting points of metals, 514
 Mendelejeff, D., 117
 Mercuric compounds, 402
 chloride, 402
 sulfide, 402, 515
 thiocyanate, 402
 Mercurous chloride, 402
 Mercury, 394, 401
 amalgams, 401
 compounds, 402
 metallurgy, 401
 occurrence, 401
 properties, 394, 401, 402
 uses, 401
 Metals, action of, on water, 53
 Metaphosphoric acid, 281
 Metasilicic acid, 314
 Meteors, 440
 Methane, 55, 125, 127, 462
 Methanol, 475
 Methyl alcohol, 475
 Metric system, 511
 Mica, 13, 313, 348
 Milk of lime, 351
 Millikan, Robert, 100
 Mirrors, 383
 Mixtures, 8, 12
 Moissan, F. F. H., 187
 Molar solutions, 233
 Molar volume of gases, 157
 Molecular weights, 103, 105
 of gases, 156
 Molecules, 4, 103
 monatomic, 9, 37, 126
 Moles, 152, 249
 Molybdenum, 431
 alloys, 434
 extraction, 434
 occurrence, 434
 properties, 434
 uses, 434
 Monazite sand, 322
 Monel metal, 453
 Monochloromethane, 474
 Monoclinic sulfur, 325
 Mortar, 351
 Moseley, H. G. J., 110
 Multiple proportions, law of, 76

Muriatic acid, 193
 Mustard gas, 185, 468

N

Naphthalene, 472
 Natural gas, 487
 Natural waters, 73
 Nebula of Orion, 178
 Neon, 9, 37, 126, 132, 175
 atom, 112
 signs, 176
 Neutralization, 209, 210, 226, 232
 heat of, 228
 Neutron, 7, 109
 Newlands, J. A. R., 117
 Nichrome, 432
 Nickel, 439, 453
 alloys, 446, 453
 compounds, 453
 occurrence, 453
 properties and uses, 439, 453
 salts, 454
 Nickel steel, 446
 Nicotinic acid, 501
 Nicotinic amide, 501
 Nitrate ion, 264
 Nitric acid, 259, 261
 preparation, 261
 properties, 263
 test for, 264
 uses, 264
 Nitric oxide, 259
 Nitrite, sodium, 261
 Nitrogen, 246
 acids, 259, 261
 atom, 112
 compounds, 246, 252, 259
 dioxide, 260
 fixation of, 247, 491
 occurrence, 33, 246
 oxides, 259
 pentoxide, 259, 260
 preparation, 248
 properties, 34, 246, 249
 tetroxide, 260
 trioxide, 260
 Nitroglycerine, 482
 Nitrous acid, 259, 261
 Nitrous oxide, 259
 Nomenclature:
 of acids and salts, 204
 of elements, 11, 12
 of hydrocarbons, 463
 Nonane, 462
 Nonelectrolyte, 214, 215
 Nonpolar compounds, 126
 Normal salts, 212
 Normal solutions, 233
 Nucleus, atomic, 108, 110
 Nylon, 3, 470

O

Octane, 462
 Octylene, 468
 Oleic acid, 481
 Open-hearth process, 444
 Orangite, 322
 Orion, 178, 179
 Orthochromatic plates, 388
 Orthophosphates, 280
 Orthophosphoric acid, 280
 Orthosilicic acid, 313
 Osmium, 455

Osmosis, 87
 Osmotic pressure, 88
 Oxalic acid, 297
 Oxidation, 45, 266, 406
 state, 268
 Oxidation-reduction equations, 266, 268
 Oxidation-reduction potentials, 514
 Oxides, 44
 of carbon, 295
 of nitrogen, 259
 Oxygen, 34, 39
 allotropic forms, 50
 atom, 112, 114
 discovery of, 34, 39
 in relation to life, 48
 liquid, 42
 molecule, 101
 occurrence, 34, 39
 preparation, 39
 properties, 34, 42
 uses of, 48, 57
 Oxygen acids of halogens, 203
 Oxyhydrogen blow pipe, 57
 Ozone, 48

P

Palau, 457
 Palladium, 455, 457
 Palmitic acid, 481
 Palorium, 457
 Panchromatic plates, 388
 Parke's process, 382, 426
 Peat, 292
 Pentane, 462
 Percentage composition, determination of, 146
 Perchloric acid, 203, 204
 Periodic acid, 204
 Periodic system, 117
 Periodic table, 103, 117, 119, 120
 Permanent hardness, 355
 Permanganates, 438
 Permutit process, 356
 Peroxide, 75
 Perrin, Jean, 100
 Persulfuric acid, 339
 Petrified wood, 314
 Petroleum, 464, 487
 pH of a solution, 234
 Phomene fire extinguisher, 304
 Phosgene, 185, 297, 475
 Phosphates, 280, 491
 tests for, 282
 Phosphine, 278
 Phosphoric acid, 278, 280
 Phosphorous acid, 278, 282
 Phosphorus, 246, 275
 acids, 278, 280
 allotropic forms, 276, 277
 atom, 113
 compounds, 278
 occurrence, 276
 pentoxide, 276
 preparation, 276
 properties, 275
 red, 277
 trioxide, 278
 white, 276
 Photochemical processes, 183, 490
 Photoelectric cell, 175
 Photoelectric effect, 175
 Photography, 385
 developing, 387
 fixing, 387

Photography (*Cont.*):

 plates, 386
 printing, 387
 Physical change, 27
 Physical properties, definition of, 26
 Pig iron, 440
 Pitchblende, 361
 Plaster of Paris, 352
 Plastic sulfur, 326
 Plate glass, 315
 Platinic chloride, 456
 Platinic hydroxide, 456
 Platinous hydroxide, 456
 Platinum, 439, 455
 black, 456
 chloride, 456
 compounds, 456
 occurrence, 455
 properties and uses, 455
 spongy, 455
 pOH, 235
 Polar compounds, 124
 Polymerization, 469
 Polymers, 198, 469
 Porcelain, 316
 Portland cement, 318
 Positron, 7
 Potassium, 164, 172
 action of, on water, 54
 atom, 112, 113
 bicarbonate, 309
 carbonate, 309
 hydroxide, 54, 173
 manganate, 438
 nitrate, 172
 occurrence, 172
 perchlorate, 204
 permanganate, 438
 preparation, 172
 properties, 172
 spectrum, 177
 test for, 172
 Potentials, oxidation-reduction, 514
 Pressure, of atmosphere, 18, 32
 Pressure cooker, 71
 Priestley, Joseph, 39
 Producer gas, 488
 Propane, 462
 Properties of matter, 25
 Propylene, 468
 Protective colloid, 242
 Proteins, 497
 Proton, 7, 108
 Prussian blue, 450
 Purification of water, 49, 74, 185
 Pyrex glass, 316
 Pyrites, 440
 Pyrolusite, 437
 Pyrophosphoric acid, 281
 Pyrosulfuric acid, 339
 Pyroxylin, 485

Q

Quartz, 13, 311, 313
 glass, 316
 Quartzite, 313
 Quicklime, 351

R

Radicals, 127
 Radioactive elements, 504
 Radioactivity, 504

Radium, 108, 344, 361, 505
 disintegration, 507
 extraction from ores, 361
 nucleus, 505
 occurrence, 361
 properties, 361
 uses, 361

Radium A, 506

Radium B, 506

Radium C, 507

Radon, 132, 506

Raoult's law, 85

Rare earth elements, 133

Rayon, 485

Reactions:

effect of concentrations on, 273

effect of surface on, 273

endothermic, 29

exothermic, 29

involving ions, 226

reversible, 60, 253, 254, 302

temperature effects on, 272

which go to an end, 60, 230

Red lead, 428

Red phosphorus, 277

Reduction, 59, 266, 406

Relative humidity, 36

Relative weights of gases, 156

Replacement reactions, 140, 195

Replacement series, 191, 406

Respiration calorimeter, 494

Reversible processes, 60, 253, 302

Rhenium, 437

Rhodium, 455

Rhombic sulfur, 325

Rhotanium, 457

Riboflavin, 501

Rotary kilns, 317

Rouge, 449

Rubber, 2, 469

Rubidium, 164, 172, 173, 175

Rust, iron, 448

Ruthenium, 455

Rutherford, Ernest, 100

Rutile, 321

S

Safety lamp, 46

Sal soda, 308

Saltpeter, 172

Chile, 169

Salts, 56, 207, 210

Sand, 313

Sandstone, 313

Saturated solutions, 79

Scheele, Carl W., 39

Scheelite, 434

Selenium, 323, 343

Sherardized iron, 396

Silica, 312

Silicates, 314

Silicic acids, 313

Silicon, 288, 311

acids, 313

atom, 113

dioxide, 312

monoxide, 312

occurrence, 311

preparation, 311

properties, 312

uses, 312

Silk, synthetic, 3, 470

Silver, 375, 382

complex ions, 392

Silver (*Cont.*):

compounds, 385

extraction from ores, 382

occurrence, 382

plating, 383, 384

properties, 375, 383, 384

sulfide, 382, 385, 515

test for, 385

uses, 383

Silver polishing, 327, 350

Slag, 441

Smaltite, 452

Smoke screen, 424

Snow crystals, 19

Soaps, 483

Soda ash, 308

Sodium, 164

action of, on water, 53

atom, 112

bicarbonate, 302, 309

bisulfate, 212

carbonate, 302, 308

chloride, 5, 168

crystal, 24

molecule, 123

solution, 217

hexametaphosphate, 281, 358

hydroxide, 54, 169

hypochlorite, 203

nitrate, 169

occurrence and discovery, 165

preparation, 165

properties, 166

silicates, 314

spectrum, 177

sulfate, 169

test for, 172, 177

tetraborate, 365

thiosulfate, 339, 387

uses, 167, 168

Solid state, 20

Solubility curves, 81

Solubility of gases, 79, 80, 82

Solutes, 78, 79, 84

effect on boiling points, 86

effect on freezing points, 86

effect on vapor pressure of solvent, 84

Solutions, 78

boiling point, 86, 216

concentrated, 82

dilute, 82

freezing point, 86, 216

molar, 232

normal, 233

pH of, 234

pOH of, 235

saturated, 79

standard, 232

supersaturated, 82

Solvay process, 308

Solvents, 78, 79

Spectroscope, 176

Spectrum, 177

analysis, 175

of Orion, 179

Speed of a reaction, 272

Spongy platinum, 455

Spontaneous combustion, 45

Stainless steel, 446

Stalactites, 357, 358

Stalagmites, 357, 358

Standard conditions, 95

Standard kilogram, 512

Standard meter, 511

Standard pressure, 95

Standard solutions, 232
 Standard temperature, 95
 Stannic compounds:
 acid, 508
 chloride, 508
 hydroxide, 509
 sulfide, 509, 515
 Stannous compounds:
 chloride, 508
 hydroxide, 509
 sulfide, 509, 515
 Starch, 484
 Stearic acid, 481
 Stearin, 482
 Steel, 443, 446
 Sterling silver, 383
 Storage batteries, 404, 412
 Stroboscope, 387
 Strong acids, 207, 219
 Strong bases, 207, 219
 Strong electrolytes, 218, 219
 Strontianite, 359
 Strontium, 344, 345, 359
 occurrence, 359
 preparation, 359
 properties and uses, 359
 Structural formulas, 459
 Structures of atoms, 107, 121, 132
 Sublimation, 69, 190
 Sucrose, 484, 496
 Sugars, 6, 484
 Sulfate ion, 338
 structure of, 128
 Sulfides, 330, 331, 515
 Sulfitcs, 334
 Sulfur, 323
 acids, 333
 allotropic forms, 325
 atom, 113
 chloride, 475
 compounds, 327, 329, 333
 dichloride, 468
 dioxide, 333
 extraction, 324
 liquid, 325
 monoclinic, 325
 occurrence, 323
 plastic, 325
 properties, 323, 326
 rhombic, 325
 trioxide, 333, 335
 uses, 327
 Sulfuric acid, 335
 action of, on metals, 337
 chamber process, 336
 contact process, 335
 properties, 337
 test for, 338
 uses of, 338
 Sulfurous acid, 334
 Supersaturation, 82
 Suspensions, 79, 237
 Sylvanite, 389
 Sympathetic ink, 453
 Synthesis, 65
 Synthetic rubber, 2, 470
 Synthetic silk, 3, 470

T

Talc, 346
 Tellurium, 323, 342, 343
 Temperature:
 effects on reactions, 272
 kindling, 45

Tempering steel, 447, 448
 Temporary hardness, 354
 Tetrachloromethane, 474
 Tetraethyl lead, 429, 466
 Tetrathionic acid, 339
 Textolite, 479
 Thermite, 370
 Thermometer scales, 512, 513
 Thiamin, 500
 Thiosulfuric acid, 339
 Thorite, 322
 Thorium, 288, 321, 322
 Tin, 421
 allotropic forms, 422
 alloys, 423
 compounds, 424
 extraction from ores, 422
 occurrence, 421
 properties, 421, 422
 uses, 423
 Tincture of iodine, 190
 Tinctures, 79
 Titanium, 288, 321, 322
 oxide, 428
 Titration, 232, 233
 Toluene, 472
 Transmutation of elements, 504, 508
 Travertine, 74
 Trichloromethane, 474
 Trithionic acid, 339
 Tungsten, 431, 434
 alloys, 435
 extraction, 435
 occurrence, 434
 properties, 435
 uses, 435
 Tungsten steel, 446
 Turnbull's blue, 450
 Tyndall effect, 237
 Type metal, 286, 427

U

Ultramicroscope, 238, 239
 Undecane, 462
 Uranium, 107, 361, 431, 435
 atom, 135

V

Valence, 127, 266, 267
 electrons, 121
 Vapor density, 156
 Vaporization, heat of, 69
 Vapor pressure, 68
 of solutions, 84, 85, 216
 of water, 68, 85, 95, 513
 Venetian red, 449
 Viscose, 485
 Visual purple, 499
 Vitamins, 499
 Voltaic cell, 409
 Volume:
 gas, 157, 160
 measurement, 512

W

Washing soda, 308
 Water, 63
 action of metals on, 53
 analysis of, 64
 boiling point, 67
 elevation of, 86

- Water (Cont.):**
 composition:
 by volume, 64
 by weight, 64
 density, 67
 electrolysis, 42, 53
 freezing point, 67
 lowering of, 86
 glass, 814
 hard, 354
 heat of fusion, 72
 heat of vaporization, 69
 heavy, 73
 of hydration, 83
 ionization, 220
 molecule, 125
 natural, 73
 occurrence, 63
 properties, 67
 purification, 74
 softening, 354, 355
 synthesis of, 65
 vapor, 35, 95
 vapor pressure, 68, 85, 513
Water-gas, 488
 method for hydrogen, 55
Water of crystallization, 83
Water of hydration, 83
Weak acids, 207
Weak electrolytes, 218, 219
Weight of one liter of various gases, 158, 514
Weights, atomic, 103, 104, 105, 110, front
 and back covers
Weights, molecular, 103, 105, 156
Welsbach mantle, 322
Wet cells, 408
White lead, 428
White phosphorus, 276
Window glass, 315
Wood alcohol, 475
Wood charcoal, 292
Wrought iron, 445
- X**
- Xenon, 37, 126**
 atom, 132
- Z**
- Zeolite, 356**
Zinc, 394
 blende, 395
 chloride, 398
 compounds, 397
 extraction from its ores, 395
 hydroxide, 397
 occurrence, 395
 oxide, 395
 properties, 394, 396
 sulfide, 395, 398
 uses, 396
Zinc blende, 395
Zircon, 322
Zirconium, 288, 321, 322



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Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
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Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150
Erbium	Er	68	167.2	Scandium	Sc	21	
Europium	Eu	63	152.0	Selenium	Se	34	
Fluorine	F	9	19.00	Silicon	Si	14	
Gadolinium	Gd	64	156.9	Silver	Ag	108	
Gallium	Ga	31	69.72	Sodium	Na	23	
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Gold	Au	79	197.2	Sulfur	S	32	
Hafnium	Hf	72	178.6	Tantalum			
Helium	He	2	4.003	Tellurium			
Holmium	Ho	67	163.5	Terbium			
Hydrogen	H	1	1.008	Thallium			
Indium	In	49	114.76	Thorium			
Iodine	I	53	126.92	Thulium			
Iridium	Ir	77	193.1	Tin			
Iron	Fe	26	55.84				
Krypton	Kr	36	83.7				
Lanthanum	La	57	138.9				
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